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THE ORIGIN AND DECOMPOSITION OF ORGANIC SULFUR COMPOUNDS UNDER GAS MAKING CONDITIONS WITH PARTICULAR REFERENCE TO THE ROLE OF THE CARBON-SULFUR COMPLEX

BY

JOHN C. HOLTZ

A

DISSERTATION SUBMITTED
TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BALTIMORE
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THE ORIGIN AND DECOMPOSITION OF ORGANIC SULFUR COMPOUNDS UNDER GAS MAKING CONDITIONS WITH PARTICULAR REFERENCE TO THE ROLE OF THE CARBON-SULFUR COMPLEX

INTRODUCTION

It is necessary to remove the sulfur compounds from raw works gas because of their deleterious effects. During combustion, these compounds form sulfur dioxide and trioxide which, in relatively small concentrations, have a toxic effect on plant life. Their attack on the mucous membranes of animals produces decided discomfort. They are also extremely corrosive to metals. In an area where a great deal of fuel containing sulfur is used the concentration of sulfur products in the air was reported to be sufficient to cause the complete destruction of iron wire screens in a period of one year. (1). Many cases of corrosion of boiler and heating plants and other combustion appliances may be traced directly to the action of the sulfurous and sulfuric acids formed from the sulfur compounds in the flue gases. (2). Because of the extensive domestic and industrial use of gas, the removal of sulfur compounds is therefore of much importance, not only to the gas industry, but also to the general public in the areas supplied.

Crude gas contains two classes of sulfur compounds. These are commonly designated as inorganic and organic sulfur compounds. The inorganic sulfur consists chiefly of hydrogen sulfide, which is easily removed from the gas with iron oxide or one of the processes of liquid purification. None of the organic sulfur is removed from the gas in the ordinary processes of purification and this class of sulfur compounds form an interesting subject for further research and development.

The organic sulfur consists chiefly of carbon disulfide and this compound generally amounts to about 80 per cent of the total sulfur in organic combination. (3, 4). The remaining 20 per cent is composed of various compounds which have received but very little study by the research workers in the gas and fuel field.

Researches recently published (5) have shown that organic sulfur compounds existing in manufactured gas undergo a slow decomposition to form deliquescent, corrosive sulfur salts while being handled in the works and distribution equipment. These salts, through the corrosion which they stimulate and the attendant deterioration of meter diaphragms which they may cause, are a primary source of some of the

most important depreciation of the capital investment of a gas company.

Catalytic processes for the production of alcohols and motor fuel from water gas involve the use of catalysts, many of which may have their activity seriously diminished or even entirely destroyed by the organic sulfur contained in water gas. (6). This is true also of the proposed processes for enriching water gas by catalytic methanation.

The sulfur content of gas distributed by public utilities is rigorously limited by controlling state bodies. Since no process is at present available for the economic removal of the organic sulfur in gas, in order that it may meet the service requirements imposed, the gas industry has been obliged to use fuels which contain only small amounts of sulfur. High sulfur fuels are available at a lowered cost, but cannot be used because of the high organic sulfur content of the resulting gas. If an economic process for removing the organic sulfur were provided, or if some method of controlling the organic sulfur could be established from a knowledge of its mode of formation, a lowering in fuel costs should follow.

A survey of the literature on the subject of the organic sulfur in gas reveals that the principal efforts have been directed toward its removal and that but relatively little work has been done with regard to the suppression of its formation. The formation and decomposition of organic sulfur compounds under gas making conditions was selected as the subject of this dissertation not only because so little information on this topic was available, but also because such information appeared to be essential to progress in other phases of the general sulfur problem in gas making.

PART I—HISTORICAL

CHAPTER I

THE OCCURRENCE OF ORGANIC SULFUR IN GAS AND STUDIES OF ITS CONTROL

The organic sulfur content of gas is limited by law to a certain maximum concentration. Craven and Dunkley (7) report that this maximum concentration in many states of the United States is 30 grains per 100 cubic feet of gas. In a few states it is limited to 20 or 25 grains. The gas industry has, therefore, used low sulfur content fuels which yield gas that will meet these requirements. The survey by these authors showed that the organic sulfur concentrations in the crude gases of a number of plants varied from 4.9 to 20.7 grains per 100 cubic feet when the sulfur content of the coal used varied from 0.55 to 1.2 per cent. The survey included both coal and water gas. The water gas was usually found to contain a lower concentration of organic sulfur. It was concluded that the sulfur in the gas, both organic and inorganic, bears no definite relation to the sulfur in the fuel used. It was also noted that high concentrations of inorganic sulfur in the gas are not necessarily accompanied by high concentrations of organic sulfur. Such conclusions pointed very definitely to the need for further research on the sulfur compounds in gas and particularly research on their mode of formation.

Organic Sulfur in Coal Gas

The organic sulfur content of gas in England is not limited by law and Meade (8) reports 35 to 50 grains per 100 cubic feet as the average concentration in coal gas and 10 to 15 grains in water gas. The table given below shows the variation of the organic sulfur in coal gas with the volume of gas made per ton of coal. The volume, of course, increases with increasing temperature of carbonization.

Gas made, cubic feet per ton of coal (9)	Organic sulfur concentration, grains per 100 cubic feet
6896	13.91
8370	19.16
9431	26.75
10772	36.93
11620	44.17

Meade also reports (10) that the chief organic sulfur constituent of coal gas other than carbon disulfide is thiophene.

Other surveys have also reported the variations in the concentration of organic sulfur compounds in commercial gas. One comparative survey of the gas produced from commercial plants (11), including both horizontal and vertical retorts, indicated that the gas from vertical retorts generally contains a lower concentration of carbon disulfide. This is attributed to the fact that in vertical retorts the gas is usually subjected to less overheating than in horizontal retorts. Parr (12) has observed that no carbon disulfide is contained in commercial gas if the temperature of carbonization has not exceeded 800° C. He mentions the theory that carbon disulfide results from the interaction of hydrogen sulfide and highly heated carbon.

This formation is sometimes partially controlled by the addition of lime to the coal being carbonized. Meade reports (13) that the addition of 1.5 to 2 per cent of lime to coal resulted in lowering the organic sulfur of the gas to 21.5 grains, and increased the volume of gas and the yield of ammonium sulfate per ton of coal. No data were given regarding the sulfur content of the coal used.

A complete study of the sulfur distribution during coal carbonization has been made in the Gas Engineering Laboratories of the Johns Hopkins University (3) using a 400-pound direct-fired stop-ended horizontal retort. The experimental apparatus really comprised a small coal gas plant. The coal used in the study contained 1.94 per cent total sulfur. The following factors were found to have an effect on the total organic sulfur in the gas: (a) temperature, (b) weight of charge, and (c) the addition of lime. An increase in the temperature of carbonization from 1500 to 1900° F. caused the organic sulfur to increase from 11 to 28 grains per 100 cubic feet. If varying weights of coal were charged to the retort at a given temperature it was found that the organic sulfur in the gas changed. The gas from a charge of 200 pounds of coal contained about 28 grains, from 300 pounds 23 grains and from 400 pounds 17 grains. The addition of lime to the charge was found to decrease the organic sulfur in the gas, the greatest effect being noted toward the end of the carbonization period.

A small scale investigation of the distribution of sulfur during the carbonization of coal has been reported by Powell (14). His experiments did not show any carbon disulfide in the gas. As the apparatus used was very small it was concluded that the time necessary for secondary reactions, involving the formation of carbon disulfide, did not exist under these experimental conditions. An investigation of this hypothesis was later carried out by Huff (15), using an apparatus of the same size and noting particularly the conditions for the formation of carbon disulfide. It was found that if the coal was coked slowly no carbon disulfide was formed, but that carbon disulfide was formed if the rate of coking was

rapid. The secondary reactions of the carbon disulfide with hot coke were also examined, and Huff found that these reactions, under his experimental conditions, promoted the elimination of carbon disulfide rather than its formation.

Organic Sulfur in Water Gas

The discussion has so far been directed largely to the formation of organic sulfur during the carbonization of coal. The manufacturers of carburetted water gas have also given some consideration to this formation. In order to utilize a high-sulfur high-coke oil for carburetting the gas, a modified carburetted water gas set has been designed (16). The design was based on the theory that the carbonaceous matter deposited on the checker brick of the set reacted with hydrogen sulfide to form the organic sulfur. However, the designer reported that this carbonaceous material does not become active in such reactions during the run in which it is formed, but only during subsequent runs, when it has become thoroughly heated to incandescence. Therefore, if the carbon is burned off immediately after the run in which it is formed, less organic sulfur should appear in the gas. To accomplish this result the set is modified by the addition of an extra hot valve which permits the carbon to be burned off the checker brick during the blasting of the generator. The set has been operated for a year using a fuel oil having a specific gravity of 0.9776, 4.7 per cent of sulfur and a coke residue of 16.9 per cent (17). The gas obtained from the set contained about 520 grains of hydrogen sulfide and 40 grains of organic sulfur per 100 cubic feet. Close regulation of the temperature of the checker brick was found to be very important. If the temperature became too high the effect was the same as though the checker brick had not been cleaned of carbon. When the temperature was properly regulated, a large proportion of the sulfur in the oil does not appear in the gas at all. No trouble was experienced from plugging of the carburetter because of the high coke residue of the oil used.

Another modification of a water gas set which has received much attention is the "backrun" process (18). In this process, the down run steam of the ordinary water gas generating cycle is admitted to the set at the top of the superheater. From this point the steam passes through the superheater and carburetter to the generator. From the bottom of the generator the gas is conducted directly to the washbox by a special pipe. This "backrun" steam becomes very highly superheated within a very short distance from the top of the superheater and then reacts with and removes the carbon from the checker brick. The inventors claim as an advantage of the process that, because of the clean checker brick in the set, poorer grades of oil containing coke and sulfur can be utilized for carburetting the gas without producing excessive concentrations of organic sulfur (19).

CHAPTER II

THE ASSOCIATION OF CARBON AND SULFUR IN A SOLID PRODUCT

Any extended study of the organic sulfur problem in gas making inevitably leads to a consideration of possible reactions between carbon and sulfur. In the last chapter mention has been made of the theory that carbon disulfide resulted from the interaction between carbon and the sulfur of hydrogen sulfide. This at once suggests the possibility of other reaction products and an examination of the literature shows that such products have been recognized, the chief form being some type of solid association.

As early as 1807, Berthelot (20) investigated the reaction of sulfur vapor with carbon at a red heat. The carbonaceous residue remaining at the conclusion of the experiment was examined and found to contain sulfur in some form other than free sulfur.

Stein (21) has described the behavior of carbon disulfide when treated at a red heat. His description stated that the carbon disulfide was first broken down to deposit free carbon and form free sulfur. When the experiment was continued in the presence of this deposited carbon the carbon disulfide passed through the heated zone without any apparent decomposition. The investigator reported it was probable that the carbon disulfide did not pass through the heated zone without decomposing but that it decomposed and then formed again from the products of decomposition.

Other investigators (22), studying the formation of a subsulfide of carbon, C_3S_2, by passing carbon disulfide vapor through a quartz tube heated to a temperature of 900 to 1200° C., report that the reaction leaves a carbonaceous residue. An analysis of this residue showed that it contained sulfur. It did not, however, differ in appearance from finely divided carbon.

Action of Solvents

Such sulfur containing carbons were examined by Mixter (23). He was able to obtain these synthetically in a number of different ways and found that the products contained varying percentages of sulfur. He examined the action of solvents such as benzol and carbon disulfide on these products and found that the sulfur could not be removed by this treatment. He concluded from these observations that the sulfur must be held by the carbon in chemical combination.

Wibaut, working with Stoffel (24), became interested in the interaction of carbon and sulfur during an investigation of the behavior of sulfur during the coking of coal. The coke was found to contain a portion of the sulfur of the coal combined with the iron present and another portion of the sulfur combined with the carbon. The sulfur combined with the carbon was designated as organically bound sulfur. In a further study (25), sulfur was heated with carbon and the residue from the treatment was extracted with solvents. The solvents used were benzol, toluol, carbon disulfide and sulfur monochloride. In all cases the loss of sulfur caused by the action of the solvents was negligible.

Effect of Heat Treatment

A later paper by Wibaut and La Bastide (26) presented a very thorough study of this combination. Sulfurous-carbons were made by passing sulfur vapor over heated amorphous carbon, such as sugar charcoal, at temperatures up to about 1000° C. and also by heating the sulfur and charcoal together in closed tubes at temperatures up to 600° C. When these sulfurous-carbons were formed by passing sulfur vapor over heated charcoal, carbon disulfide was found in the vapor products, but no other compounds were detected. When the sulfur and carbon were heated together in closed tubes to a temperature of 500° C. pressure was developed in the tubes. It was necessary to open the tubes and release the pressure in order to prevent the tubes from bursting. These were then resealed and the heating continued to 600° C. No examination of the products released from the tubes was reported.

The sulfurous-carbons obtained by these two methods contained percentages of sulfur varying between the approximate limits of 1 and 30 per cent. The largest percentage of sulfur was found in the product obtained by heating in closed tubes. Numerous attempts were made to produce products with identical percentages of sulfur by the same treatment of two different portions of material, but these were unsuccessful.

The sulfurous-carbons containing high percentages of sulfur could be decomposed when heated slowly to 1100° C. in a vacuum. The decomposition gave free sulfur and carbon disulfide and seemed to take place in steps. The initial formation of carbon disulfide took place when the carbon was reheated to only 600° C. Raising the temperature of decomposition to 800° C. produced more carbon disulfide and after the evolution of products ceased at this temperature more carbon disulfide could be obtained by raising the temperature to 1000° C. After continued heating of the residue to a temperature of 1100° C. It was still found to contain some sulfur. The percentage of sulfur remaining was less than 3 per cent.

A form of sulfurous-carbon has also been obtained by Cuisa (27), who heated thiophene-tetra-iodide to a temperature sufficient to decompose it. The residue was called thiophene graphite and was found to contain 37.6 per cent of sulfur. As this percentage of sulfur corresponds very closely

to that required for the theoretical compound C_4S it was thought that such a compound had been prepared. However, Wibaut (28) repeated these experiments and found that some iodine remains in the residue which behaves in general in the same manner as his sulfurous-carbons.

Effect of Hydrogen

Wibaut and La Bastide (26) treated in a stream of hydrogen some of their residues obtained by heating the sulfurous-carbons to 1100° C. The residues were maintained at temperatures from 500 to 700° C. and it was found that they could be substantially freed from sulfur by the action of the hydrogen, leaving almost pure carbon. The sulfur contained in the residues could be collected quantitatively as hydrogen sulfide in the exit gases.

This action of hydrogen has also been reported by Powell (29) to take place on the organically combined sulfur in coke at a temperature of 500° C. or higher. The desulfurizing action of the hydrogen takes place with the formation of hydrogen sulfide. The action was increased as the temperature of the coke increased, and decreased as the percentage of hydrogen in the scrubbing gas decreased. Further observations indicated that the action was reversible. That is, if the concentration of sulfur in the gas was sufficiently high the coke took up sulfur from the gas, while if it was low the gas took up sulfur from the coke.

This behavior of the sulfur toward hydrogen led Powell (30) to investigate the form of the organic sulfur in coke by a phase rule study. Hydrogen was passed over a carbon residue containing sulfur, formed by heating sulfur and sugar charcoal together, maintained at various temperatures above 500° C. The vapor pressure of the sulfur in the exit gas was obtained by determining the concentration of hydrogen sulfide it contained. The concentration of hydrogen sulfide in the gas should remain constant during the decomposition of any chemical compound of the carbon and sulfur which might be present. No regions of constant sulfur vapor pressure were observed on any of the isothermal curves obtained. A study of the isothermal curves led to the conclusion that the sulfur in the complex existed in two forms: (a) adsorbed sulfur and (b) sulfur in solid solution or some other form which could not be differentiated from solid solution by this method. The method was also applied to a coke obtained from coal and a region of constant sulfur vapor pressure was found on the isothermal curve. This region was attributed to the presence of ferrous sulfide in the coke.

Effect of Metals

The retention of sulfur by coke in the presence of iron has been studied by Lissner (31). He coked samples of coal mixed with iron and examined the coke in a stream of hydrogen at elevated temperatures and noted the amount of sulfur retained by the coke after this treatment.

The coke retained more sulfur as the amount of iron increased. An examination of coals containing a high percentage of ash led to the conclusion that the ash constituents may exert an influence similar to iron. No gaseous decomposition products other than hydrogen sulfide were reported.

Formation From Sulfur Dioxide

Residues of carbon containing sulfur have also been prepared by allowing sulfur dioxide to react with carbon. Fischer and Pranschke (32) passed sulfur dioxide over heated carbon for periods of about 24 hours, after which the carbon was cooled in sulfur dioxide. The carbon was prepared as charcoal from a number of different sources. The residues were found to contain percentages of sulfur varying from 1.4 to 37.5 per cent. The percentage of sulfur was affected by the temperature at which the reaction was allowed to proceed. The data did not lead to any generalizations and the exit gases were not examined for gaseous products which may have been formed by the reaction.*

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*Remark: A study of the data of Fischer and Pranschke shows that in several different cases, utilizing the same initial sample of charcoal, the sulfur content of the residues began to decrease if a temperature of 550° C. was exceeded during their formation. Wibaut and La Bastide (26) (see page 18) have shown that their sulfurous-carbons decompose at 600° C. to give carbon disulfide. It is suggested from these facts that the formation of carbon disulfide may begin at a temperature of about 550° C.

CHAPTER III

COMPOUNDS CONTAINING CARBON AND SULFUR

As stated in the introduction, the most important organic sulfur compound in manufactured gas is carbon disulfide, and this compound may constitute as much as 80 per cent of the total organic sulfur (3, 4). Some reference to its formation and properties is therefore an important part of this dissertation. The constitution of the compounds making up the remaining 20 per cent of the organic sulfur is not well known and very little data are available concerning this subject. A review of pertinent information taken from the literature on other sulfur compounds which may possibly occur is also presented.

Carbon Disulfide

That carbon disulfide may be produced by allowing sulfur vapor to react with incandescent coke has been known for many years, and this is at the present time probably the most important method of synthesis practiced commercially. The forms of this process have been described a number of times and are generally so familiar that it is not necessary to consider them in detail here. However, there are a number of other processes which are of interest because the reactions involved may occur under gas making conditions.

While free acetylene probably does not exist in appreciable amounts during the manufacture of gas for public distribution, reactions between sulfur and unsaturated hydrocarbons are to be expected. The formation of carbon disulfide from acetylene and free sulfur reported by Capelle (33) is therefore worthy of mention. A patent (34) describing this reaction has been issued. This patent also claims the production of carbon disulfide by the reaction of acetylene and heated metallic sulfides such as iron sulfide. A somewhat analogous reaction between antimony sulfide and coke has been reported by Lampadius (35). Carbon disulfide was formed when these materials were heated together.

The production of carbon disulfide by the passage of hydrogen sulfide over incandescent coke has been patented (36). This reaction has been rather generally accepted as that responsible for the carbon disulfide found in manufactured gas.

A series of investigations (37) of the decomposition of carbon oxysulfide have reported carbon disulfide among the products of the decomposition. The formation of carbon disulfide takes place very slowly according to the reaction:

$$2COS = CO_2 + CS_2.$$

This formation of carbon disulfide is favored by low temperatures, the maximum formation occurring at about 600° C., at which temperature the equilibrium mixture contains 43 per cent of carbon disulfide plus carbon dioxide, 6 per cent of carbon monoxide and free sulfur, and 51 per cent of carbon oxysulfide. No trace of any other sulfur compounds was detected during these experiments.

This reaction is also used commercially (38) for the production of carbon disulfide. A mixture of carbon monoxide and sulfur vapor is passed over a catalyst of iron, wood charcoal or active charcoal maintained at temperatures varying from 400 to 600° C. The gaseous mixture resulting from this treatment contains 10 to 15 per cent carbon disulfide, 65 to 70 per cent carbon oxysulfide, and about 20 per cent carbon dioxide. The carbon disulfide is recovered from this mixture and the remaining gases are recirculated.

The formation of carbon disulfide by the reaction of sulfur dioxide and carbon was reported by Berthelot (39). This reaction was studied by Rassow and Hoffmann (40) specifically for the formation of carbon disulfide when wood charcoal was used as the carbon. The maximum formation of carbon disulfide was obtained from 850 to 900° C. At this temperature 35 per cent of the sulfur in the sulfur dioxide was transformed into carbon disulfide, 55 per cent into carbon oxysulfide, and 10 per cent appeared as free sulfur. The gaseous products of the reaction also contained carbon monoxide and a small amount of carbon dioxide. A patent (41) covering the use of this reaction as a method for producing carbon disulfide commercially has been granted.

The measurement of the equilibrium constant for the formation of carbon disulfide from sulfur vapor and carbon was attempted by Koref (42). He passed the sulfur vapor over the carbon at several temperatures about 900° C. and measured the carbon disulfide contained in the products of the reaction. The data obtained were thermodynamically consistent *inter se* and were used in certain calculations, the results of which were later shown by other investigators to be inconsistent with other known facts.

Lewis and Lacey (43) investigated the reaction:

$$SO_2 + 2CO = S + 2CO_2.$$

in an attempt to obtain data leading to the calculation of the free energy of sulfur dioxide. Among the reaction products were found carbon oxysulfide, carbon disulfide and a gaseous sulfur compound which interfered with the determination of carbon monoxide when the iodine pentoxide method was used. After removal of the carbon oxysulfide and carbon disulfide from the reaction products the other sulfur compound in the gas was decomposed by passing the remaining gaseous products over heated copper. This compound was thought by them to be carbon monosulfide, but was not studied further. These investigators criticized Koref's

results and attributed the inconsistency of his work to the fact that he did not take into account the formation of any compounds of carbon and sulfur other than carbon disulfide.

Carbon Oxysulfide

The formation of carbon oxysulfide has already been mentioned incidentally (37, 38, 40 and 43). This compound may be expected in gaseous mixtures containing appreciable quantities of oxygen and sulfur compounds of any type, when such mixtures are subjected to temperatures ranging from 500 to 1000° C. In an investigation of the reaction:

$$4CO+2SO_2=4CO_2+S_2.$$

Ferguson (44) observed that carbon oxysulfide was formed by secondary reactions, but its presence could not be detected in the reaction products if the reaction was carried out at a temperature above 1000° C. A few of the possible reactions leading to the formation of carbon oxysulfide are:

$$2CS_2+2C=2CO_2+S_2$$

$$S_2+C=CS_2.$$

$$S_2+CO_2=COS+CO+SO_2.$$

$$S_2+2CO=2COS.$$

$$CS_2+CO_2=2COS.$$

Carbon Monosulfide

The existence of carbon monosulfide was first announced by Baudrimont (45). He reported its formation by several methods, but claimed that the best yields were obtained by the passage of carbon disulfide vapor over platinum or pumice stone heated to redness. These observations were confirmed by Persoz (46), but Playfair (47) claims that he could not reproduce Baudrimont's experiments.

Low (48) obtained a polymeric form of carbon monosulfide as a brown powder from the action of sunlight on carbon disulfide in a closed tube. Sidot (49) produced this form of carbon monosulfide in the same manner and verified its composition by analysis.

Dewar and Jones have done a great deal of work on carbon monosulfide. Their first study (50) dealt with its formation from nickel carbonyl and thiophosgene in the cold. The reaction is assumed to occur according to the equation:

$$xNi(CO)_4+xCSCl_2=xNiCl_2+4xCO+(CS)_x.$$

The carbon monosulfide was obtained as a brown powder which was carefully washed free from nickel chloride. Analyses of this powder

gave good checks with the theoretical percentages of carbon and sulfur in carbon monosulfide. This form of carbon monosulfide can be decomposed by heating to a dull red heat. Among the products of decomposition at this temperature are carbon disulfide and a carbon-like residue containing sulfur. This sulfur could be removed by passing hydrogen over the residue at a red heat.

These same investigators also examined the effect of a silent electric discharge on carbon disulfide vapor at a reduced pressure (51). This treatment of carbon disulfide yields a gaseous compound which at —80° C. polymerizes rapidly into a brown powder identified as carbon monosulfide. If the gaseous products of the experiment were cooled to —210° C. a white solid was obtained which polymerized very slowly but which finally changed to a brown powder. When the temperature of the white solid was allowed to increase the rate of polymerization increased rapidly and the change was accompanied by a detonation and flash of light. The rate of polymerization was retarded by the presence of a foreign gas.

Carbon Subsulfide

Another interesting compound of carbon and sulfur is the carbon subsulfide having the formula C_3S_2. This compound was first reported by Von Lengyel (52), who obtained it by passing carbon disulfide vapor through a carbon arc. The subsulfide was recovered as a red liquid which slowly polymerized at ordinary temperatures. This subsulfide was also prepared by Arctowski (53), who passed carbon disulfide vapor through a heated quartz tube. Both of these methods were subsequently verified by Stock and Praetorius (54). When heating carbon disulfide in an empty quartz tube the subsulfide could be obtained in a temperature range from 900 to 1200° C., the best yield being obtained from 1000 to 1100° C. At temperatures higher than those at which the best yield was obtained it was observed that more carbon disulfide was decomposed but apparently in some other way than reduction to the subsulfide. The presence of carbon in the quartz tube apparently prevented the formation of the subsulfide.

When the subsulfide was formed by distilling carbon disulfide through an arc it was found that the yield could be increased if one of the electrodes was made of or contained a high percentage of metal. Thus, the best yields were obtained when one electrode of the arc was formed from antimony plus 7 per cent of carbon. Later, a detailed report (55) of the formation of the subsulfide in a zinc arc was published. The action of the metal in increasing the yield of the subsulfide was interpreted as proving that it resulted from the reduction of the carbon disulfide.

That the subsulfide exists as a deep red liquid, which slowly polymerizes at ordinary temperatures to yield a black solid has already been mentioned. This solid polymer can be decomposed at a dull red heat, yielding carbon disulfide and carbon subsulfide and leaving a black

carbon-like residue containing 39 per cent of sulfur. The other physical properties of the subsulfide have also been determined (54). Its melting point is —0.5° C. and its vapor pressure has been measured up to 90° C., at which temperature it is 48 mm. of mercury. It may be of interest to note that the analogous compound of carbon and oxygen has also been identified and described (56).

Other Sulfur Compounds

Another investigation of the effect of a silent electric discharge on carbon disulfide was reported by Losanitsch (57). He claims that the brown powder obtained in this way is a polymer of carbon disulfide rather than carbon monosulfide. However, the later work of Dewar and Jones, already commented upon (51), confirming the monosulfide formula, seems to deserve more weight since the phenomena occurring seem to have been more closely observed. Losanitsch also investigated the action when other substances were present with the carbon disulfide. Thus, when hydrogen or hydrogen sulfide were present a powder was obtained which analyzes to the general formula $3CS_2 \cdot 2H$. Compounds of this general type were also obtained when carbon monoxide, ethylene, acetylene or benzene were present. An examination of the product obtained from carbon disulfide and ethylene showed it to be a polymer of the formula $(C_2H_4S)_6$. The mechanism of this reaction is thought to be first the formation of ethyl mercaptan, which then condenses with itself and splits off hydrogen.

The action of nascent hydrogen on liquid carbon disulfide in the presence of zinc is reported (58) to yield a substance crystallizing as needles and subliming at 150° C. Analysis of the substance showed it to be a multiple of the general formula CHS. This substance could be decomposed at 200° C. to yield a new one which crystallized as quadratic prisms the composition of which was not determined.

Mittasche (59) reports that when hydrogen saturated with carbon disulfide vapor is passed over reduced nickel at a red heat a compound is obtained. The composition of the material was not determined, but its melting point was found to be between 65 and 70° C.

Sulfur Compounds in Gas

The discussion of the compounds containing carbon and sulfur has so far been limited to compounds reported in the literature without regard to their actual identification in commercial gas. In fact, other than carbon disulfide, thiophene is the only compound to be definitely determined (60) in gas. However, the boiling points of the following compounds indicate that their vapor pressure is great enough that they may be detected in a sample of gas if they are present under saturated conditions: carbon oxysulfide, methyl and ethyl mercaptan, methyl and ethyl sulfide, and possibly thiophenol. It is interesting to note that certain

of these compounds have been identified in coal tar oils and must therefore exist in coal gas under some conditions of retort or oven operation. The compounds found in coal tar are: mercaptans containing either an alkyl or an aryl group (61, 62); the alkyl thio-ethers (61); thio-naphthene (63); thio-napthene-2-methyl (64); thiophene (65); methyl-thiophene (66); and diphenylene sulfide (67). It follows that the compounds listed above should be considered in research involving the identification of sulfur compounds in gas, particularly in coal gas. However, this problem will entail a great deal of work, since these compounds must be present in amounts far less than the concentration of carbon disulfide. Micro-chemical methods of analysis must be developed to permit the use of a sample of gas of usual size for the determinations.

CHAPTER IV

PROCESSES FOR THE REMOVAL OF ORGANIC SULFUR FROM GAS

In attempting a solution of the organic sulfur problem, the principal efforts have been directed toward the removal of organic sulfur from the gas. A great number of processes have been proposed, and several have been applied at gas manufacturing plants, but up to the present time none has possessed all of the features necessary for complete commercial success. In order to complete the survey of the organic sulfur research relating to the gas industry, a short review of the more important work of this nature is presented in this chapter.

The methods to be considered may be conveniently separated into the following general classifications:

1. Decomposition by the application of heat.
2. Catalytic decomposition with and without the use of steam.
3. Surface adsorption methods.
4. Washing processes.
5. Chemical processes.

1. Decomposition by the Application of Heat

The methods falling in this class are somewhat similar to those in the second class in that both require the application of some heat for successful operation. In this first will be included those processes in which the inventor does not attribute the purification of the gas to any catalytic action.

The methods in this class are dependent upon the reaction:

$$CS_2+2H_2=C+2H_2S.$$

The presence of hydrogen in the gas being treated is an essential feature of the successful operation of the process.

Among these the most successful method is the Pabst reheating system (68), which has been applied at the Portland (Oregon) Gas Company. The gas, in this process, is freed from hydrogen sulfide in the usual oxide purifiers and then passed through a superheater filled with refractory checker material maintained at a temperature of 1200° F. The checker material gradually becomes coated with a carbonaceous deposit from the decomposition of the carbon disulfide and the efficiency

of decomposition slowly decreases. Another superheater is provided for the purification of the gas while the first one is being regenerated by burning off this carbonaceous material. The hydrogen sulfide formed during the decomposition is subsequently removed from the gas by passage through oxide purifiers. This process is said to remove about 70 per cent of the total organic sulfur.

2. Catalytic Decomposition With and Without the Use of Steam

Catalytic purification has been in general more successful than that in the other classes. A metallic catalyst, with some material added as a promoter, is employed, at temperatures ranging from 250 to 1200° F. The reactions are:

$$CS_2+2H_2=2H_2S+C$$

and

$$CS_2+2H_2O=2H_2S+C\cdot O_2$$

The best known of these processes is that of Carpenter (69) and Evans (60). The gas, in this process, is freed from hydrogen sulfide and then passed over a catalyst, which is principally nickel maintained at a temperature of 800° F. The catalyst is slowly covered with a carbonaceous deposit which renders it inactive. When this occurs, the process is interrupted and the catalyst revivified by passing air over it. It is claimed that 80 per cent of the organic sulfur in the crude gas is converted into hydrogen sulfide.

This process was studied in a detailed laboratory investigation (70), in which it was established that the active catalyst was the subsulfide of nickel, Ni_3S_2, a compound which had been previously identified. The catalyst caused the oxygen compounds of the gas to react with hydrogen sulfide to form carbon oxysulfide if the gas was not freed from the hydrogen sulfide before it was passed over the catalyst. When used on coal gas, the principal sulfur compound remaining in the gas was thiophene. Other sulfur compounds, not identified, were present. The velocity of the gas over the catalyst could be increased if a metallic oxide was mixed with the nickel to serve as a promoter. The use of chromium—, thorium—, aluminum—, or beryllium-oxide as promoters has been claimed in a patent (71). The process was employed by the South Metropolitan Gas Company of London for some time.

A more recent patent (72) claims a catalyst which is a mixture of metals and metallic oxides, one of the metals of the said mixture melting at a temperature below that used for the treatment of the gas. This temperature is from 400 to 600° C. Permanent activity of the catalyst is claimed by virtue of fine subdivision of the catalyst secured by admixture of suitable inorganic substances. The catalyst presented as an example is formed from equal parts of lead chromate and copper oxide. Substantially complete removal of all organic sulfur compounds is claimed.

A patent by Fischer (73) claims the use of a gold or silver catalyst in the presence of hydrogen. Silverized asbestos can be used at temperatures from 200 to 300° C.

Another patented process (74) uses three purifiers to secure complete removal of the sulfur from gas. The first purifier for removing hydrogen sulfide contains nickel oxides supported in pumice clinker or porous earth and is maintained at a temperature of 250° C. This is followed by a second purifier containing copper or iron oxide in which hydrogen sulfide is formed by decomposition of the organic sulfur if the gas contains steam. The third purifier contains nickel oxides and removes the hydrogen sulfide formed in the second purifier. The catalysts are regenerated with air or water gas containing steam.

Cooper (75) has reported a substantial reduction of the organic sulfur in gas by reheating with steam present. The amount of organic sulfur decomposed could be increased by using metallic copper as a catalyst at a temperature of 500° C. This process was later reported (76) to be unsatisfactory because of the temperature required. At the same time the use of calcium oxide at temperatures from 200 to 250° C. was reported to cause a reduction in the total organic sulfur of 30 to 40 grains per 100 cubic feet when the gas contains about 50 grains of organic sulfur per 100 cubic feet.

A number of processes in which iron oxide is used as the catalyst have been reported, the chief difference between them being the temperature at which the treatment is carried out. This catalyst requires a certain amount of steam to be mixed with the gas before its passage over the catalyst. Rideal and Taylor (77) claim the addition of metallic oxides to the iron oxide catalyst and use the catalyst at temperatures ranging from 550 to 1200° F. Fulweiler (78) uses an active iron oxide at 450° F.; Guillet (79) an ordinary iron oxide purifier at 250° F., and Anderson (80) uses the same iron oxide purifier, but at about 125° F. Guillet claims that only the carbon disulfide is destroyed when iron oxide is used, the other sulfur compounds remaining unchanged by this treatment.

Teune (81) finds that the use of a spent oxide containing free sulfur is not practical for removing carbon disulfide from gas. The use of yellow ocher has been patented (82), as have aluminum oxide, bauxite and magnesite (83).

Another catalyst is reported (84) under development by Beckman. This catalyst, at the time of writing, had only been examined in the laboratory and as the patents on the process are not yet issued the nature of the catalyst has not been revealed. It is claimed that the laboratory examination of the catalyst showed from 76 to 92 per cent removal of the organic sulfur at temperatures about 700° F. The removal of the organic sulfur was increased by decreasing the size of the particles of catalyst. In the laboratory the size was from 20 to 50 mesh.

3. Surface Adsorption Methods

The use of active charcoal for removing organic sulfur from gas has been reported by Wanner (85). The purifying effect of the charcoal seems to be due only to surface adsorption and is increased by an increase in the active surface of the charcoal. The charcoal is regenerated for further use by reheating. Adams (86) claims the use of 70 pounds of granulated animal or wood charcoal to purify 12,000 cubic feet of gas containing 35 grains of sulfur and 6 grains of naphthalene per 100 cubic feet. Another process (87) claims the use of peat coke and still another (88) the charcoal obtained by carbonizing hard woods. The removal of hydrogen sulfide from the gas before it is passed over the charcoal allows a more complete removal of the organic sulfur compounds. Another report (89) examines the behavior of charcoal in removing the sulfur compounds from coke oven gas under a number of experimental conditions, including the admixture of air with the gas and the recovery of the charcoal when regenerated by the action of gases at 500° C.

The action of silica gel in removing sulfur compounds from a kerosene solution containing pure compounds is reported by Waterman and von Tussenbrock (90). Silica gel has also been patented as an adsorbent for the organic sulfur of gas (91). The silica gel, heated to about 200° C., is used in two layers and is impregnated with a small percentage of iron or copper oxide or both before being used. The gas to be treated is subjected to a preliminary heat treatment at 450° C.

4. Washing Processes

Several processes have been proposed in which the organic sulfur compounds of the gas are removed by absorption in a suitable washing medium. Experiments at Halifax (92) report the removal of 75 to 85 per cent of the organic sulfur by scrubbing the gas with a paraffin oil. The oil circulation is maintained at a high rate because of the high vapor pressure of the carbon disulfide. Light oil removal is effected at the same time and the wash oil is regenerated by steam distillation. A later report (93) on this process states that the efficiency of organic sulfur removal in plant equipment was found to be 50 per cent.

Removal of the organic sulfur has been accomplished by washing the gas with an ethyl alcohol solution (94) at temperatures of —5 to —15° C. The alcohol vapors remaining in the gas after this treatment are recovered by washing with a recirculated water solution in which the alcohol concentration is maintained below 10 per cent by volume. This water solution, when mixed with the alcohol solution, causes the benzol scrubbed from the gas to separate from the resulting mixture. The separated benzol contains any organic sulfur and naphthalene that was scrubbed from the gas. The alcohol is recovered for reuse in the process, which claims a removal of 80 per cent of the organic sulfur contained in the gas.

Weissenberger and Schuster (95) discuss the desired properties of a good gas washing medium and propose the use of tetra-hydronaphthalene. Data are cited to show the suitability of this material for recovery of benzol, light paraffin oils and carbon disulfide from gas.

5. Chemical Processes

The processes in the chemical classification are those in which the organic sulfur is removed from gas by reacting chemically to give a non-volatile salt or a product which is retained in a solution.

One of the reactions utilized is that of carbon disulfide with an alkaline hypochlorite solution (96). During an investigation of the suitability of such a solution for removing hydrogen sulfide from gas it was observed that 46 per cent of the organic sulfur also was removed (97). A later investigation (98) found that 67 per cent removal of organic sulfur could be easily secured, and this percentage could be increased by increasing the time of contact of the gas with the solution. The removal of the organic sulfur is accomplished chiefly by oxidation. An important objection to the method is the liberation of chlorine which takes place.

One of the processes for removing organic sulfur from gas is known as the "Athion" process (99). The "Athion" compound is the salt of an alkali and cellulose and is used in contact with the gas in a finely divided form like iron oxide. Carbon disulfide reacts with this compound to form cellulose xanthogenate and formyl cellulose. This reaction accomplishes the removal of 75 per cent of the total organic sulfur. Carbon dioxide also reacts with the "Athion" compound, decomposing it, and so must be removed from the gas before this is passed over the "Athion" compound. It is stated that 10 tons of the material will take up 1.25 tons of carbon disulfide or purify about 35,000 M. cubic feet of gas made from German coals. The use of the process is covered by patents (100).

Another process (101) uses a solution of amines containing metallic oxides. The chief form of the organic sulfur removed from the gas is the carbon disulfide. This compound reacts with the amines to form alkyl-dithio-carbamic acid salts.

A similar patent (102) claims the use of an aqueous solution of amines in the presence of an alkali or alkaline earth hydroxide, hydrosulfide or sulfide, or of substances such as cellulose xanthates which are capable of readily liberating hydrosulfides. Weiss (103) has also patented the use of an aqueous solution of amines, such as aniline, for removing organic sulfur from gas and the results of a laboratory investigation of the process have been reported by Prince (104). The commercial application has been criticized because the process must bear either the cost of the amines vapors lost in the gas stream or the cost for acid washing the gas in order to recover these vapors.

Minot (105) proposes to remove the carbon disulfide from gas by washing with a solution of the polysulfides of sodium. The process is said to be used on coal gas where the ammonia of the gas reacts to form

ammonium sulfide which will react with carbon disulfide to form ammonium thio-carbonate. The process also removes carbon dioxide and cyanogen from the gas.

In the early days of the gas industry lime was used to remove hydrogen sulfide from the gas. Some of the carbon disulfide is also removed by this treatment. The carbon disulfide is taken up by the lime in a moist state, the absorption being more rapid if the gas is free from carbon dioxide. The hydroxy-hydrosulfide of lime is said to be the active absorbing agent, although the chemistry of the process is open to some question (106).

Several reviews of the removal of organic sulfur from gas have been published. Matwin (107) reports the results of a laboratory investigation of several of the processes. Ab-Der-Halden (108) and Powell (109) present summaries of the processes actually in use. Witzeck (110) also has presented a series of articles on this subject.

CHAPTER V

THE DETERMINATION OF CARBON DISULFIDE AND TOTAL ORGANIC SULFUR IN GAS

Methods for determining carbon disulfide have been referred to extensively in the literature. As it will be impossible to give even a short abstract of these articles, only those applying to the determination of carbon disulfide in gas will be considered here.

Determination of Carbon Disulfide

Hofmann (111) reported the formation of an addition compound when carbon disulfide is added to tri-ethyl-phosphine. The compound is composed of one mol of carbon disulfide and one mol of tri-ethyl-phosphine, and is characterized by beautiful red prismatic crystals. This reaction was used by him to prove the presence of carbon disulfide in coal gas (112) and by Wibaut and La Bastide (26) to detect the presence of carbon disulfide in the decomposition products of their sulfurous carbons. Wibaut (113) has studied the reaction and reported the properties of the red crystals.

The same reaction was used by Hegel (114) for the determination of carbon disulfide in a gas. The gas consisted chiefly of carbon disulfide, hydrogen sulfide and carbon dioxide. It was first dried over calcium chloride and then bubbled through two successive 45 cc. portions of a 1 per cent solution of tri-ethyl-phosphine in dry fat free ether chilled to —10° C. The precipitate formed in the tri-ethyl-phosphine solution was collected in a Gooch filter, dried in a vacuum at room temperature and finally weighed.

Another reaction utilized for the determination of carbon disulfide is the formation of an xanthate from carbon disulfide and an alcoholic solution of caustic potash. Macagno (115) has studied the reaction and has used it to determine carbon disulfide in air. The carbon disulfide was estimated quantitatively by adding an excess of copper sulfate to the acidified xanthate solution and collecting the precipitate of cupric xanthate. This precipitate was then oxidized to cupric oxide and the amount of carbon disulfide calculated from the weight of oxide. As an alternate method the acidified xanthate solution was titrated with a standard copper sulfate solution using potassium ferro-cyanide as an outside indicator.

Harding and Doran (116) also studied this reaction, since there seemed to be some question as to the ratio of carbon disulfide in the xanthate. A measured amount of copper acetate solution, in excess of that required to precipitate the carbon disulfide as cupric xanthate, was added

to the acidified solution of xanthate. The precipitate was then filtered off and the excess copper in the filtrate determined by adding potassium iodide to the solution and titrating the iodine formed with a sodium thiosulfate solution. This general method was then applied to the determination of carbon disulfide in illuminating gas (117) by scrubbing the gas, freed from carbon dioxide, hydrogen sulfide and dried with sulfuric acid, with an alcoholic solution of caustic potash. The xanthate solution obtained was then treated as described for the estimation of carbon disulfide. Results secured by running parallel tests on city gas agreed closely.

The method of Harding and Doran was examined by Huff (118), who found that the formation of cupric xanthate did not take place readily when the copper solution was added to xanthate solutions of low concentration. Furthermore, definite endpoints were not obtained in the iodine titration when the concentration of copper salts in the solution was low. These difficulties were overcome by redesigning the gas scrubbing equipment so that the gas could be brought into intimate contact with two successive portions of one cubic centimeter of saturated alcoholic potash solution. The formed xanthate was carefully collected with the aid of a small amount of wash water, acidified with acetic acid and a measured excess of copper sulfate solution added. This solution was allowed to stand, preferably overnight, to insure complete precipitation of the cupric xanthate and then filtered. The filtrate was evaporated to dryness on a water bath and the residue taken up with 5 cc. of a 1:15 solution of hydrochloric acid. One gram of powdered potassium iodide was then added and the liberated iodine was titrated with a standard sodium thiosulfate solution. The proper control of the acidity and concentrations in all steps of the method was found to be very important. The conditions were so defined by Huff that the method can be used to detect 0.02 mg. of carbon disulfide qualitatively. For the quantitative determination of carbon disulfide a sample of about two liters of gas is used requiring only one-half an hour for passage through the described apparatus.

Selivounoff (119) describes a method essentially like that of Harding and Doran, except for the treatment of the xanthate. The xanthate solution is evaporated to about one-half its original volume, exactly neutralized to phenolphthalein with acetic acid and titrated with 0.002 N copper sulfate solution in the presence of a low concentration of guaiac resin.

The brilliant yellow color of cupric xanthate has been utilized by Desy (120) in developing a colorimetric method for the estimation of carbon disulfide in gas. The color produced in a definite volume of solution from the carbon disulfide in a measured volume of gas is matched against the color produced in the same total volume of solution by addition of a measured volume of a standard solution of xanthate. The volume of the standard xanthate solution required to match the color produced by the carbon disulfide from the gas is a measure of the carbon disulfide

in the gas. The standard xanthate solution used on a 500 cc. sample of gas is described.

Determination of Total Organic Sulfur

The methods considered above have been specific for the determination of carbon disulfide. The usual determination of total organic sulfur in gas is known as the Referees' method (121). This consists essentially of burning a measured volume of gas in a small burner, washing the products of combustion with a dilute ammonia solution in an air condenser to retain the sulfur compounds. The liquors are collected, made acidic, and the sulfur compounds oxidized to sulfates with bromine. The sulfates are precipitated as barium sulfate which is collected on a filter and weighed. The objections to the method are chiefly the rather large quantities of gas, the length of time required for the complete determination and the fact that it cannot be used with accurate results where the air is contaminated with sulfur products.

The Bureau of Standards has developed a method (122), essentially the same as the Referees' method, in which the combustion products are scrubbed by bubbling through a 5 per cent solution of potassium carbonate. The apparatus is so arranged that the air required for combustion is scrubbed free from sulfur products in order to avoid any error from this source. Furthermore, the gas sample can be burned at a somewhat more rapid rate and the time required for the determination reduced. The principal disadvantage of the method is the considerable amount of accessory apparatus it requires.

A very much simpler method for determining the total organic sulfur has been developed in the research laboratories of the Department of Gas Enginering of the Johns Hopkins University (123). The gas, which must contain hydrogen, is passed over a platinum spiral heated to incandescence. The hot platinum spiral transforms the organic sulfur into hydrogen sulfide. The hydrogen sulfide in the gas leaving the spiral is titrated with iodine in a Tutwiler burette. The amount of hydrogen sulfide found is a direct measure of the organic sulfur contained in the original gas sample. If gas is allowed to stream over the heated platinum spiral continuously the determination of the hydrogen sulfide in the exit gas can be made in about 5 minutes, but when the spiral has not been heated for some time the gas should be allowed to pass over the heated spiral for about 30 minutes before attempting to obtain a result.

Another method has been reported (124) in which the hydrogen sulfide, carbon disulfide and remaining organic sulfur compounds are determined in the same sample of gas. The gas to be analyzed is first metered, then passed through two bottles containing 5 per cent potassium hydroxide solution followed by a dehydrator containing calcium chloride, then through glass wool. The dehydrated gas is passed through two absorption bulbs containing a nearly saturated solution of potassium hydroxide in absolute alcohol which removes any carbon disulfide

from the gas. The residue is burned in an A. S. T. M. sulfur lamp (125) and the products of combustion scrubbed with a dilute solution of sodium carbonate. When the desired amount of gas has been passed the whole apparatus is flushed out with nitrogen. The solutions used for the absorption of the different forms of sulfur are then collected and titrated to determine the amounts of sulfur existing in the gas in each form. The potassium hydroxide solution, used for absorption of the hydrogen sulfide, is acidified, and the hydrogen sulfide regenerated by this treatment is titrated with an iodine solution. The carbon disulfide is found by direct titration of the acidified xanthate solution with an iodine solution. The iodine reacts with the potassium xanthate to form dixanthogen and potassium iodide. The remaining organic sulfur is calculated from the excess of sodium carbonate found by titrating with hydrochloric acid. For a gas containing about 15 grains of carbon disulfide per 100 cubic feet, about 1.5 cubic feet of gas should be used and passed through the apparatus at the rate of about one-third of a cubic foot per hour, although accurate results are claimed when only 6 to 8 liters of gas are used. The rate of gas passage is, of course, dependent upon the type and number of absorption bulbs used in the train.

PART II—EXPERIMENTAL

CHAPTER VI *

THE CARBON-SULFUR COMPLEX. QUALITATIVE EXPERIMENTS

Noting that carbon disulfide was formed during carbonization experiments only when high rates of heating were employed, Huff (15) suggested that the heterogeneous character of the coal caused local concentrations high in sulfur, which, when heated suddenly, became chemically active in the formation of carbon disulfide. This carbon disulfide was swept rapidly out of the retort before it could be decomposed by contact with carbon free from sulfur. At the same time, the need of additional inquiry into the explanation of the formation of carbon disulfide was stressed.

Use of Oil

In such an inquiry, the formation of carbon disulfide during the cracking of oil should be of interest since the sulfur compounds of oil are probably very uniformly dissolved in the remaining constituents of the oil. This affords an experimental condition quite unlike that prevailing in coal, the heterogeneous makeup of which is recognized.

For the qualitative preliminary experiments a gas oil having the properties given in Table I was used (unless otherwise noted).

Experimental Apparatus

The apparatus used for cracking this oil is shown in Figure 1. The oil is fed to the cracking tube, A, at a controlled rate from the burette, B. The connection, C, was used to balance the pressure in the burette against that in the cracking tube. The cracking tube, A, was an inclined vitreosil tube 36 inches long, ⅞-inch internal diameter and ⅛-inch wall thickness. The heat required for the cracking was furnished by the electric furnace, D, which had an effective heating length of 12 inches. The furnace temperature was measured by means of the base metal thermocouple, E, placed at the center of the furnace between the cracking tube and the furnace wall. The gas from the cracking passed through the tar filter, F, which contained absorbent cotton. Any liquid tar which separated was collected in the trap, G. The gas, free from tar vapors, was finally collected in the gasometer, H. The oil was cracked at the rate of 2 cc. in 5 minutes and the gas col-

*Some of the experimental material contained in this chapter has already been published by Huff and Holtz, Ind. Eng. Chem. *19*, 1268 (1927); Proc. A. G. A. 1927, p. 1431.

TABLE I

PROPERTIES OF THE GAS OIL USED

Data on Original Oil

Color	Black
Viscosity	2.77 at 77° F. (25° C.)
Water	Trace
Sulfur	3.61% by weight
Specific gravity	0.9123
Flash point	220° F. (104° C.)
Burning point	245° F. (118° C.)

Distillation Data

Temperature °F.	Temperature °C.	Per Cent Off By Volume	Per Cent Off By Weight	Specific Gravity	Description of Fraction
–300	–149	....	....	.....	.....
300–350	149–177	....	....	.....	.....
376–400	191–204	0.4	0.3	0.769	Colorless
400–450	204–232	2.8	2.5	0.817	Colorless
450–500	232–260	9.5	8.8	0.839	Colorless
500–550	260–288	15.2	14.7	0.869	Very light yellowish green
550–600	288–316	16.6	16.4	0.892	Light yellowish green
600–650	316–343	17.0	17.0	0.904	Yellowish green
650–700	343–371	17.6	17.8	0.916	Dark yellowish green
700–722	371–383	18.7	19.1	0.920	Reddish brown
Coke...	.....	....	1.12		
Total..	.....	97.8	97.72		

REMARKS: Rate of distillation: 3 c.c. per minute.
See Gas Chemists' Handbook, 1929, 3rd ed., pp. 74–78.

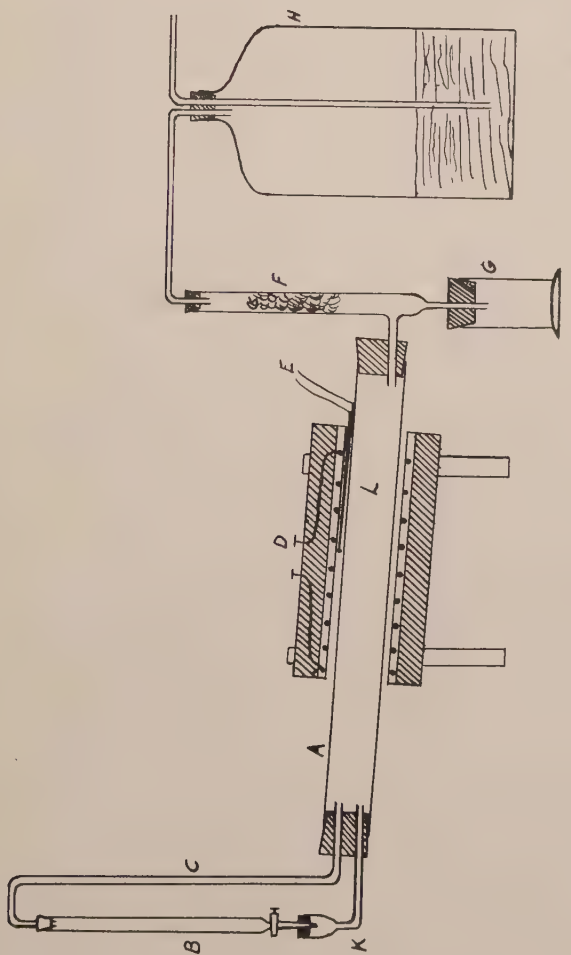

FIGURE 1

APPARATUS FOR QUALITATIVE EXAMINATION OF FORMATION OF CARBON DISULFIDE*

* THIS DRAWING IS NOT TO SCALE

lected in the gasometer was examined for carbon disulfide by the method of Huff (118).*

Effect of Cracking Temperature on Carbon Disulfide Formation

The initial experiments were directed toward an examination of the carbon disulfide content of the gas obtained from cracking the high sulfur oil at various temperatures. The gas produced at a furnace temperature of 1200° F. during a two-hour run did not show the presence of carbon disulfide when a two-liter sample was analyzed. Gas produced under the same conditions, with the exception of the furnace temperature, which was raised to 1350° F., showed a very definite precipitate of cupric xanthate in the test for carbon disulfide. A gas sample produced at 1800° F. gave a very heavy precipitate of cupric xanthate.

These experiments showed very positively that carbon disulfide could be formed from a gas-making material, initially homogeneous, and emphasized the importance of temperature effects in this production. However, no information was available to indicate whether this carbon disulfide was produced by scission during the degeneration of complex organic sulfur compounds in the oil or by synthesis from carbon and sulfur vapor produced by such degeneration.

Formation of Carbon Disulfide From Hydrogen Sulfide During Cracking of a Sulfur Free Oil

In order to examine this question of scission or synthesis, several liters of sulfur free oil gas were prepared by cracking a medicinal oil ** at 1500 to 1600° F. The gas from this oil gave no test for hydrogen sulfide, but for experimental purposes a sufficient quantity of this compound was added to the gas to give it a concentration of 400 grains of hydrogen sulfide per 100 cubic feet of the final mixture. After this mixture had stood for some time, to allow mixing by diffusion, it was passed through a clean cracking tube, by means of a connection substituted at the point K in Figure 1, while additional medicinal oil was being cracked at a furnace temperature of 1500 to 1600° F. The resulting gas showed no trace of carbon disulfide, but an important amount of hydrogen sulfide had disappeared. Allowing for the dilution of the original gas mixture with the gas produced by cracking the additional oil, it was calculated that the resulting mixture should have a concentration of 140 grains of hydrogen sulfide per 100 cubic feet if no loss of hydrogen sulfide took place during the cracking. The resulting gas actually showed by test a concentration of only 70 grains of hydrogen sulfide per 100 cubic feet, thus establishing an important loss of sulfur to either retort carbon, tar or volatile organic sulfur compounds other than carbon disulfide. This experiment was repeated with the concentration of hydrogen sulfide in the original gas raised to

*See page 24.

**The oil used was Nujol as supplied by the Standard Oil Company of New York. This oil caused no stain on bright metallic copper during 72 hours contact.

over 3000 grains per 100 cubic feet of gas. The finished gas gave a heavy precipitate of cupric xanthate, showing an important concentration of carbon disulfide. An important loss of hydrogen sulfide was again noted.

From these experiments it was established that sulfur introduced as hydrogen sulfide might be converted to carbon disulfide under some conditions of cracking. However, under the conditions tested, the conversion favored the loss of sulfur to products other than carbon disulfide. Since a carbonaceous deposit and some tar were formed under the cracking conditions, it was not possible to decide whether the appearance of carbon disulfide was due to the interaction of sulfur and carbon or to the addition of sulfur by the cracked oil products, followed by subsequent scission.

Reaction of Incandescent Carbon and Hydrogen Sulfide

To examine the interaction between carbon and hydrogen sulfide a cartridge of sugar charcoal about two inches long was placed in the cracking tube at the center of the furnace. Nitrogen (containing 0.2 per cent oxygen as an impurity) was used as the base gas. Sufficient hydrogen sulfide was added to this (base gas), using the method of Gollmar (126), to give a concentration of 200 grains of hydrogen sulfide per 100 cubic feet. A glass wool filter was used to remove any spray from the gas stream before it entered the heated tube containing the charcoal, which was maintained at a furnace temperature of about 1550° F. No hydrogen sulfide could be detected with a lead acetate stain paper when the paper was placed in contact with the gas first issuing from the tube containing the charcoal, but a distinct odor of sulfur dioxide was noticed for a short time. This was probably due to reaction of the hydrogen sulfide and oxygen occluded by the charcoal. The odor of sulfur dioxide soon disappeared, but for a short time longer no hydrogen sulfide could be detected in the outlet gas. Following this interval, the concentration of hydrogen sulfide in the outlet gas gradually increased, but the tests for carbon disulfide remained negative until some 20 liters of gas had passed over the charcoal at a rate of 3 to 4 liters per hour. At that time carbon disulfide was detected in the outlet gas, and its presence confirmed in all subsequent tests. For a short time its concentration appeared to increase, then remain approximately constant. Analysis of the charcoal, which was free from sulfur at the beginning of the experiment, showed that it contained 2.8 per cent of sulfur.

This experiment was repeated in substantially the same manner except that the charcoal was broken into smaller pieces, thereby presenting a more extensive surface to the action of the hydrogen sulfide in the gas stream. Under these conditions, no carbon disulfide was detected in the exit gas until 32 liters of gas had passed over the charcoal. The charcoal was analyzed, after 64 liters of gas had passed over it, and showed a sulfur content of 5.5 per cent.

Previous experimental work (15) has shown that under certain conditions hydrogen sulfide in coal gas failed to give carbon disulfide when passed over heated coke, and the carbon disulfide already present was partially decomposed.

The results of the experiments described above suggest that carbon surfaces, initially free from sulfur, when exposed to sulfur-containing gases at temperatures encountered in gas making, possess for a time the property of adsorbing sulfur from those gases, thereby assisting in the decomposition of the sulfur compounds contained in the gases. As these carbon surfaces gradually attain saturation, this property diminishes and carbon disulfide is ultimately given off from such surfaces.

Decomposition of Carbon Disulfide by Heated Surfaces

The tendency for heated surfaces, such as surfaces of refractory material, to decompose organic sulfur compounds in gas is well known. After a time, these surfaces lose this property. This loss of decomposing power is generally attributed to the accumulation of carbon on these surfaces, and in accordance with this explanation it is found that the decomposing properties of the surface are restored by burning off the carbonaceous deposit. In such experiments in the Gas Engineering Laboratories at the Johns Hopkins University, these carbonaceous deposits have always contained sulfur which was, of course, also removed by the burning off process. It is suggested that the loss of decomposing power is not due merely to the presence of carbon upon the surface, but rather to the gradual saturation of this carbon with sulfur.

To examine this theory the high sulfur gas oil was cracked first in an empty tube and then in a tube containing a 4-inch cartridge of clean pumice, 8 to 20 mesh size. The position of the pumice cartridge is indicated at L in Figure 1. In this position the cartridge should be at the same temperature as the inside of the cracking tube. With the fresh cartridge in place it was possible to increase the furnace temperature from 1200 to 1350° F. without producing sufficient carbon disulfide to be detected in the collected gas. This absence of carbon disulfide in the gas is attributed to the decomposing action of the hot terminal surfaces of pumice upon which the requisite concentration of sulfur and carbon for the formation of carbon disulfide had not yet been attained.

That carbon free from sulfur possessed a property similar to clean pumice was demonstrated by replacing the pumice cartridge with one of coke purged with hydrogen at 1000° C. Again no carbon disulfide was formed at a cracking temperature of 1350° F. With continued use, however, the concentration of sulfur on the carbon may be expected to rise and carbon disulfide will ultimately be given off by such a surface. A continuation of the experiment verified this prediction, carbon disulfide was ultimately found in the exit gas.

This delay in the formation of carbon disulfide over cracking surfaces has been noted in the operation of carburetted water gas plants.

Klein (16), in his discussion of the formation of carbon disulfide from high-sulfur, high-coke oils in water gas carburetion, says, "When using a high-coke oil, a large part of the coke is deposited on the checker brick. During the run in which it is deposited, the coke is too cool to react with the hydrogen sulfide. If permitted to remain, however, it becomes incandescent during the succeeding blow and on the following run is active in the formation of carbon disulfide."

Granting that the formation of carbon disulfide may be accelerated by increased temperatures on the reacting surfaces, the delay in its appearance encountered in the above described experiments cannot be explained by the assumption that it is caused by external temperature changes. It is therefore suggested that the delay is caused by the adsorption of sulfur by the carbon surfaces and that no carbon disulfide is produced by these surfaces until a certain requisite concentration of sulfur has been reached.

There has been no evidence to show that the carbon disulfide is produced by a simple reaction between hydrogen sulfide and carbon.

The Carbon-Sulfur Complex

A number of experimenters have noted the association of carbon and sulfur as a solid residue unchanged in appearance from the carbon of which it was formed.* Powell (30), by his phase rule study of these solid products, has shown that they do not contain an appreciable amount of any definite compound of carbon and sulfur. Wibaut and La Bastide (26) have shown definitely the varying concentration of sulfur in these various solid products. They have also shown that, once formed, these products are broken down on being heated to high temperatures to give carbon disulfide and to leave a residue which still contains some sulfur. A consideration of the results of these investigators, together with the results of the experiments described herein, leads to the conclusion that this solid product of carbon and sulfur is a complex, and that at least a part of the carbon disulfide in manufactured gas results from the decomposition of this solid complex. This complex and its action in the formation of carbon disulfide appears to be analogous with a complex of carbon and oxygen in the combustion of carbon.

The Carbon-Oxygen Complex

The existence of the carbon-oxygen complex was first pointed out by Rhead and Wheeler (127). Their conception of what takes place during combustion is as follows: " . . . each oxygen molecule that comes into collision with the carbon becomes 'fixed,' . . . for the present it is sufficient to assume that several carbon molecules hold one oxygen molecule, in bond as it were, and do not allow it to escape in conjunction with one of their atoms. A considerable evolution of heat takes place

*See Chapter II, page 7.

during this attachment of oxygen molecules, so much so that some of them eventually acquire sufficient energy to seize hold of a carbon atom and depart with it as carbon dioxide. Some of them become torn apart in the process—become atomized—and leave the carbon molecule as carbon monoxide.

"The formation of a complex, and partial decomposition as fresh oxygen molecules become attached, goes on until the carbon becomes saturated, the products of combustion during this period, a comparatively short one, being CxOy, CO_2 and CO. After the carbon has become saturated there is an alternate formation and decomposition of the complex . . . "

Further Experimentation

If this type of a formation applies to the synthesis of carbon disulfide, there should also appear other compounds of carbon and sulfur. In the foregoing experiments the presence of sulfur compounds other than carbon disulfide was not tested for. Lewis and Lacey (43), working under somewhat similar conditions, have noted the existence of some other volatile compound containing sulfur and have suggested that a carbon-sulfur complex or a volatile carbon sulfur compound was responsible for the inconsistencies noted in the thermodynamic study of Koref (42). To examine further the properties of the complex and the possible existence of volatile carbon sulfur compounds other than carbon disulfide the experiments were extended. A quantitative procedure was developed to permit the determination of the presence of volatile sulfur compounds other than carbon disulfide, together with the amount of sulfur which they contained.

CHAPTER VII

QUANTITATIVE EXPERIMENTS ON THE HYDROGEN SULFIDE-CARBON-CARBON DISULFIDE EQUILIBRIUM

The method adopted for the quantitative examination of the hydrogen sulfide-carbon-carbon disulfide equilibrium consisted essentially in the passing of gas containing hydrogen sulfide, at a controlled rate of flow, over sugar charcoal which was maintained at a definite temperature. The gases issuing from contact with the sugar charcoal were examined for carbon disulfide and the amount of sulfur contained in other organic sulfur compounds formed by the reaction.

Apparatus

The apparatus used in these experiments is shown in Figure 2. The bulk of the gas stream was drawn from the cylinder, A, in which it was stored under pressure, through the pressure reducing valve, B, and then through a weighted governor, C. The rate of gas flow was indicated by the flow meter, D, and was controlled by varying the weight load on the governor, C. The gas then passed into the vitreosil tube, E, which contained heated copper gauze to remove any free oxygen from the gas. The heat for the copper gauze was furnished by the electric furnace, F. The temperature of this furnace was measured by a base metal thermocouple, G, placed between the furnace wall and the vitreosil tube. This temperature was maintained above 750° F. throughout all experiments with the aid of the small lamp bank, H.

The gas stream, thus freed from oxygen, was then passed through acetic acid in the bottle, I, and then through an aqueous solution of sodium hydrosulfide in the bottle, J. By controlling the concentration of the acetic acid the concentration of hydrogen sulfide produced in the gas by the reaction with sodium hydrosulfide could be controlled.* The stream was then dried in a tower containing phosphorous pentoxide, K, or completely saturated at this point by contact with water. The concentration of the hydrogen sulfide in the gas was determined by analyzing samples withdrawn from the sampling tee, L. The gas then passed over heated charcoal.

The charcoal, placed at the point M, formed a reaction cartridge about three inches long in the vitreosil tube, N, of ⅞-inch inside diameter. This vitreosil tube was 15 inches long and was sealed to the 3 mm. vitreosil capillary tube, O, which was 12 inches long. The charcoal was held in place against this seal by another piece of 3 mm. vitreosil capillary tubing, P, which was 15 inches long. This piece of tubing

*This is Gollmar's method. See reference (126).

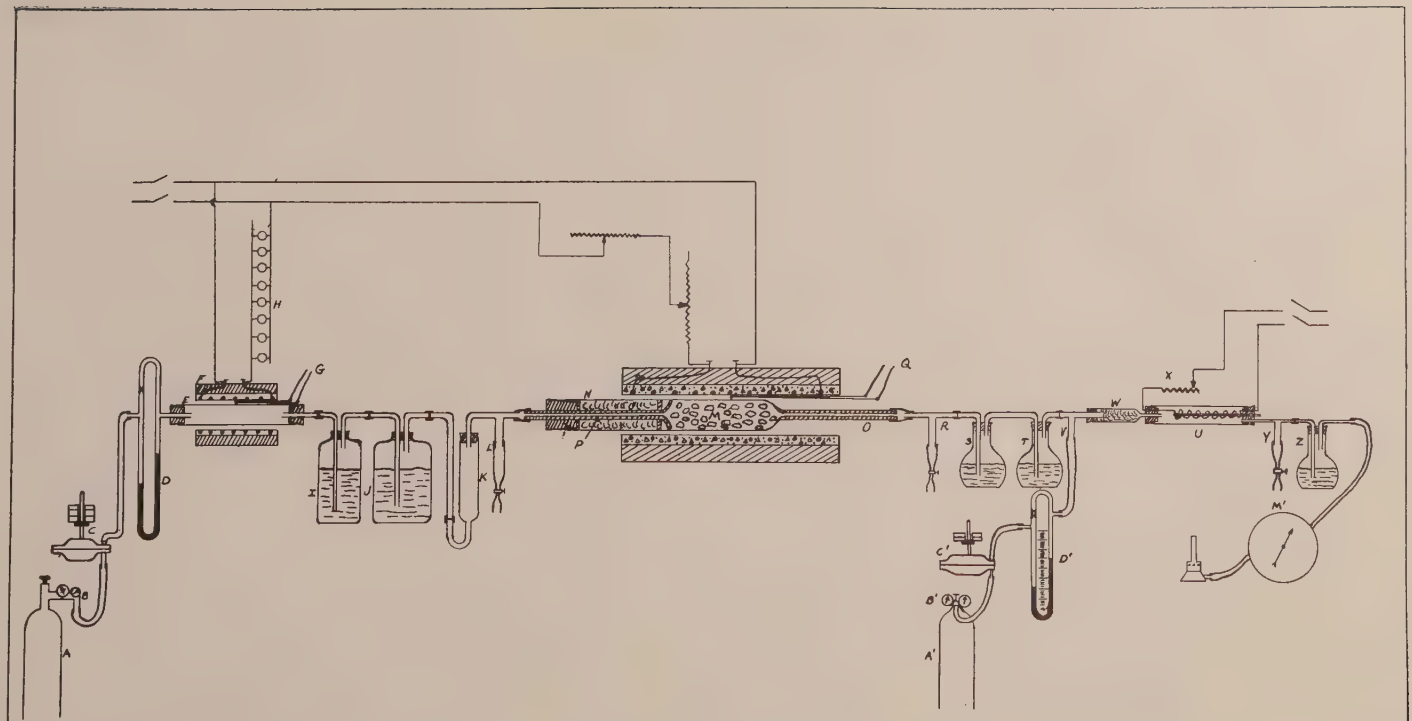

FIGURE 2 - APPARATUS FOR QUANTITATIVE EXAMINATION OF THE HYDROGEN SULFIDE - CARBON - CARBON DISULFIDE EQUILIBRIUM*

* THIS DRAWING WAS NOT MADE TO SCALE

was flared out at one end to fit snugly into the larger tube, N, and retain the charcoal. After the charcoal was in position the space between the tubes, P and N, was tightly packed with shredded asbestos, washers of sheet asbestos being used to prevent the asbestos from coming into contact with the charcoal and to hold the asbestos in position at the open end of the tube. The connection was made gas tight by slipping a rubber stopper over the extended end of the capillary tube. This stopper fitted the larger tube tightly. Placing the charcoal in this manner caused the incoming gas to reach the charcoal at a high velocity, thus minimizing decomposition of the hydrogen sulfide before it reached the charcoal. The products of any reaction were also removed at a high velocity, thus minimizing reversion before the gases had been cooled. These conditions permitted the determination of equilibrium data.

The charcoal was heated by an electric furnace, the temperature of which was indicated by the thermocouple, Q. The temperature was controlled by means of rheostats. Under the conditions encountered, the temperature could be maintained within a maximum variation of $\pm 10°$ C., which was deemed to be sufficiently accurate.

Samples were taken at the tee, R, to determine the hydrogen sulfide and carbon disulfide in the gas leaving the charcoal. The exit gas stream was scrubbed with a 5 per cent solution of potassium hydroxide in the bottle, S, and then by saturated cadmium chloride in the bottle, T. These solutions serve to remove any residual hydrogen sulfide, but do not remove any carbon disulfide. The saturated solution of cadmium chloride served as an indicator of the efficiency of removal of the hydrogen sulfide by the caustic. No experiment was continued after a yellow precipitate of cadmium chloride indicated that hydrogen sulfide was passing the caustic bottle. The gas, thus freed from hydrogen sulfide, was then passed over the heated platinum spiral, U, in order to convert the total remaining sulfur compounds to hydrogen sulfide.

Since these remaining sulfur compounds cannot be transformed into hydrogen sulfide except in the presence of hydrogen, a carefully measured quantity of this gas was added continuously to the stream at the tee, V. The hydrogen required was drawn from the cylinder, A′, where it was stored under pressure. The flow from the cylinder was controlled by the pressure reducing valve, B′, and the weighted governor, C′. The rate of flow was indicated by the flow meter, D′. To insure a well mixed gas passing over the spiral, the gases were passed through the plug of shredded asbestos, W, which was about 3 inches long. The asbestos also served as a filter to remove any residual free sulfur which would also be converted into hydrogen sulfide by the spiral.

The spiral may be made from 36 to 48 inches of No. 30 B. & S. gauge platinum wire and is heated from a 110-volt supply. The temperature of the spiral at any given current flow is affected by the distance

between the coils of the spiral, the constituents present in the gas being analyzed * and the rate of gas flow. To control the temperature of the spiral, the rheostat, X, is used in the spiral circuit.

Samples drawn from the tee, Y, were used to determine the hydrogen sulfide formed by the decomposition of the organic sulfur. The gas stream was then scrubbed with strong caustic in the bottle, Z, to remove hydrogen sulfide and then metered in the 0.1 cubic foot wet test meter, M'. The residual gases were burned to prevent an accumulation of hydrogen in the room.

Experimental Procedure

The charcoal used in these experiments was prepared from granulated can sugar.** A quantity of sugar was placed in an open refractory dish and heated with a Fisher burner until all of the volatile matter appeared to be given off. The solid carbonaceous residue which remained was broken into small pieces of the desired size. A portion of this residue was placed in a vitreosil tube, ⅞-inch inside diameter, and heated for 6 hours at a temperature ranging from 1000 to 1100° C. During the heating a slow stream of hydrogen was passed through the tube. The resulting charcoal possessed good strength and a gas analysis of nitrogen passed over it during one of the experiments showed no trace of oxygen containing compounds which might have been formed from oxygen occluded in the charcoal. The charcoal was free from sulfur and contained only 0.1 per cent ash.

This charcoal was packed into the reaction tube and the apparatus assembled. The apparatus was then purged with the gas having the composition chosen for the subsequent test and the current turned on to heat the furnaces. During the heating it was necessary to maintain a slow flow of gas through the apparatus in order to prevent the liquids in the various washing bottles from being displaced. The furnace containing the copper gauze for removing oxygen from the gas was heated first, and then the furnace heating the charcoal was brought to the desired temperature as quickly as possible. This heating period required from 1½ to 2 hours. When the charcoal furnace had attained the desired temperature the gas flow was adjusted to the desired rate and the platinum spiral heated to the proper temperature.

The concentration of hydrogen sulfide in the inlet and outlet gas from the charcoal and the total organic sulfur in the outlet gas were determined when the conditions chosen for the experiment had been attained. Thereafter, these determinations were made every hour. After the values of the total organic sulfur had remained constant for several hours, samples of the outlet gas were drawn and the concentration of the carbon disulfide determined. The experiments were continued for about 12 hours.

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*The most important of these constituents is hydrogen, which has a high thermal conductivity.

**Domino cane sugar as supplied commercially by the American Sugar Refining Company was used without further purification.

The normal pressures in the apparatus were about 24 inches of water at the copper gauze and about 6 inches at the charcoal. This normal pressure increased somewhat during the experiment as free sulfur from the dissociation of the hydrogen sulfide was deposited in the capillary tube after the charcoal. This was due to the rapid cooling of the outlet gases which prevented this sulfur from reverting to hydrogen sulfide.

At the end of the experiment the furnaces were allowed to cool by radiation while a slow stream of the gas was continued through the apparatus. When the reaction tube was cold the charcoal was removed and preserved for analysis.

Analytical Methods—Hydrogen Sulfide

The hydrogen sulfide contained in the gas at the inlet and outlet of the charcoal tube was determined in a 100 cc. Tutwiler burette. Exactly 100 cc. of gas at atmospheric pressure and room temperature was titrated with an iodine solution of such strength that 1 cc. of the solution titrated against 100 cc. of the gas represented a concentration corresponding to 100 grains of hydrogen sulfide per 100 cubic feet of gas.* This reading, without correction for temperature and pressure, was deemed sufficiently accurate.

The hydrogen sulfide contained in the gas from the spiral was titrated with the same iodine solution, using a 500 cc. Tutwiler burette. Under these conditions, 1 cc. of this iodine solution represents a concentration of only 20 grains of hydrogen sulfide per 100 cubic feet of gas. The hydrogen sulfide determined in this sample corresponds to the total sulfur contained in the organic sulfur compounds formed by the reaction.

Carbon Disulfide

The carbon disulfide in the outlet gas was determined according to Huff's method (118).**

Standardization of Solutions

The solutions required for the analytical determinations were 0.01342 N iodine, 0.01 N sodium thiosulfate, and 0.01 N copper sulfate. To determine the normality of these solutions another solution of 0.01 N potassium permanganate was prepared. The permanganate solution was standardized against pure sodium oxalate secured from the Bureau of Standards. The thiosulfate and copper sulfate solutions were titrated against the permanganate, using an intermediate solution of potassium iodide, and the iodine solution was titrated against the thiosulfate solution. After the first standardization, the copper sulfate solution was accepted as the standard, and after each experiment the normality of the other solutions was redetermined.

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*See Gas Chemists' Handbook, 1929, 3rd ed., pp. 463-6.
**See page 24.

Accuracy of Organic Sulfur Determination

The accuracy of the platinum spiral under the experimental conditions was checked by using a gas prepared to contain only carbon disulfide. A mixture of hydrogen and nitrogen, containing about 45 per cent hydrogen, was passed through a gallon of spindle oil containing carbon disulfide. Before adding carbon disulfide to the oil, it was examined and found to give no trace of any volatile organic sulfur compound. The carbon disulfide in the gas from the oil was determined according to the conditions outlined by Huff (118) to be 58 grains per 100 cubic feet of gas. This gas was scrubbed with a 5 per cent solution of potassium hydroxide and a saturated solution of cadmium chloride before it passed over the platinum spiral. The determination of the hydrogen sulfide formed in the spiral was made with a 500 cc. Tutwiler burette. The results of three consecutive determinations showed that the hydrogen sulfide from the spiral represented between 97 and 98 per cent of the carbon disulfide contained in the gas. At this concentration this accuracy represents a difference of less than 2 grains of carbon disulfide per 100 cubic feet of gas. An error of 0.1 cc. in the volume of the iodine used represents 2.24 grains of carbon disulfide, or approximately the same error.

Hydrogen

The amount of hydrogen added to the gas stream before it entered the spiral was determined by exploding samples of the gas collected after the spiral in a Morehead gas analysis apparatus.* Pure oxygen was added to the sample for explosion. Several gas samples were examined for traces of carbon monoxide as an indication of oxygen occluded in the charcoal or oxygen which was not removed by the copper gauze. The presence of this compound was never detected.

Sulfur in Charcoal Residue

When first removed from the reaction tube, the charcoal was found to have a strong odor of adsorbed hydrogen sulfide. In order to determine the sulfur content without introducing a large error from this adsorbed hydrogen sulfide, the charcoal was placed in a desiccator over sticks of sodium hydroxide and allowed to remain for at least 24 hours before an analysis for sulfur was attempted. This treatment was sufficient to reduce the concentration of hydrogen sulfide below an amount which could be detected by its odor.

Parr (128) has described the determination of sulfur in coal by fusing with sodium peroxide in a bomb, the fusion mixture being ignited by a flame applied to the outside of the bomb. It has been found that the intensity of the fusion can be controlled and rendered quiet by the addition of an increased amount of sodium peroxide. The fusion of the charcoal samples was carried out in an ordinary nickle crucible by mix-

*Gas Chemists' Handbook, 1929, 3rd ed., p. 272.

ing 0.5 gm. of finely ground charcoal with 15 gms. of sodium peroxide and igniting the mixture by placing the crucible over a Tirrill burner. A weight of about 200 gms. is sufficient to hold the crucible cover in place during the fusion, and very little, if any, of the fused material was ever found adhering to the inside of the crucible cover. The sulfate formed by the fusion was precipitated as barium sulfate in the usual manner.

Record of Results

A typical record of the data prepared from the experimental results is given in Table II. These data are all recorded directly with the exception of the item titled "Total organic sulfur in gas leaving the reaction tube—grains of H_2S per 100 cubic feet of gas." Since hydrogen must be added to the gas stream after the reaction tube before the organic sulfur in the gas can be determined with the platinum spiral the data of this item are calculated from the hydrogen sulfide contained in the gas leaving the platinum spiral and the percentage of hydrogen added. This percentage of hydrogen is also used to calculate the rate of gas flow at the charcoal, since both the gas passing over the charcoal and the hydrogen added are determined by the meter reading.

Of the two values for the concentration of carbon disulfide contained in the gas the first one, 22.7 grains per 100 cubic feet of gas, was discarded. The results of subsequent experiments indicated that this value was slightly lower than that expected when an equilibrium was fully established. The time elapsing before an equilibrium is reached depends upon the amount and the degree of subdivision of the charcoal present, since the carbon-sulfur complex is established on the surface of the charcoal.

Rate of Formation of the Carbon-Sulfur Complex

The rate of formation of the carbon-sulfur complex can be followed in the increasing concentration of the hydrogen sulfide at the outlet of the reaction tube and the concentration of the hydrogen sulfide from the decomposition of the organic sulfur at the platinum spiral. Of the two values, that of the hydrogen sulfide from the spiral is the more important criterion, since the hydrogen sulfide at the outlet of the reaction tube undergoes some reversion during cooling. The experimental data show that the concentration of carbon disulfide is not constant until the concentration of the hydrogen sulfide from the spiral becomes constant.

Check of the Equilibrium Conditions

In order to determine whether or not these experimental conditions gave equilibrium values for the concentration of the organic sulfur in the gas, another set of data were collected at this same temperature (1500° F.). These data are given in Table III. In this second experi-

TABLE II

DATA OF EXPERIMENT 6

Time	P. M. 12.15	1.15	2.15	3.15	4.15	5.15	5.25	6.15	8.15	8.40	9.15	10.15	Average
H_2S entering the reaction tube—grains per 100 cu. ft. of gas	507	517	517	517	527	517	....	517	517	....	517	517	517
H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	238	348	368	368	368	368	....	378	368	....	368	378	....
Total organic sulfur in gas at the spiral—grains H_2S per 100 cu. ft. of gas	11.9	13.9	....	17.9	19.9	17.9	....	17.9	17.9	....	17.9	17.9	....
Total organic sulfur in gas leaving the reaction tube—grains H_2S per 100 cu. ft. of gas	19.4	22.6	....	29.1	32.3	29.1	....	29.1	29.1	....	29.1	29.1	29.1
CS_2 in gas leaving the reaction tube—grains CS_2 per 100 cu. ft. of gas	....	....	....	....	....	....	22.7	....	....	29.2	....	....	29.2

REMARKS: Reacting gas: Nitrogen containing hydrogen sulfide, dried with phosphorous pentoxide.
Temperature of charcoal: 1500° F.
Rate of gas flow at charcoal: 0.57 cu. ft. per hour.
Analysis of gas leaving spiral: 38.5% hydrogen, 61.5% nitrogen (by volume).
Sulfur in charcoal residue: 4.28% (by weight).

TABLE III

DATA OF EXPERIMENT 7

Time	H_2S entering the reaction tube—grains per 100 cu. ft. of gas	H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	Total organic sulfur in gas at the spiral —grains H_2S per 100 cu. ft. of gas	Total organic sulfur in gas leaving the reaction tube —grains H_2S per 100 cu. ft. of gas	CS_2 in gas leaving the reaction tube —grains CS_2 per 100 cu. ft. of gas
11.10 A. M.	507	258	11.9	23.4	....
12.15 P. M.	507	338	11.9	23.4	....
1.15	517	368	11.9	23.4	....
2.15	527	388	15.9	31.3	....
3.15	527	398	13.9	27.4	....
4.15	527	407	10.9	21.4	....
4.30	...	...	....	....	15.6
5.15	527	407	14.9	29.3	....
6.15	537	398	15.9	31.3	....
8.15	527	398	19.9	39.2	....
8.30	...	...	....	....	30.6
9.15	527	388	17.9	35.2	....
10.15	527	388	21.8	42.9	....
10.40	...	...	....	....	29.1
11.15	527	388	17.9	35.2	....
Average	527	...	....	35.7*	29.8

REMARKS: Reacting gas: Nitrogen containing hydrogen sulfide, dried with phosphorous pentoxide.

Temperature of charcoal: 1500° F.

Rate of gas flow at charcoal: 0.50 cu. ft. per hour.

Analysis of gas leaving spiral: 49.2% H_2, 50.8% N_2 (by volume).

Sulfur in charcoal residue: 3.13% (by weight).

* Includes values from 5.15 P. M. only.

ment more charcoal was used in the reaction tube and the rate of gas flow was decreased from 0.57 to 0.50 cubic feet per hour. The concentration of hydrogen sulfide in the reacting gas was maintained essentially constant.

The first of the three values for the concentration of carbon disulfide given in Table III (15.6) was discarded as not indicating equilibrium conditions. The close agreement between the remaining values and that in Table II shows that an equilibrium was reached.

Total Organic Sulfur Concentration

The agreement between the concentrations of the total organic sulfur formed is not so satisfactory. This variation can probably be accounted for by the difficulty encountered in controlling the addition of hydrogen to the gas stream as the experiment proceeded. The rapid cooling of the equilibrium mixture in the outlet capillary of the reaction tube caused the formation of fine particles of sulfur which passed through the washing solutions and were collected on a filter of asbestos fibre before the spiral and ultimately increased the back pressure in the apparatus. This increased back pressure affected the rate of hydrogen flow far more than the rate of nitrogen flow. Furthermore, since equilibrium was established, changes in the rate of flow should not affect the results when these changes take place in the rate of flow of the gas passing through the charcoal, and therefore no variation is detected in the concentration of the carbon disulfide because these samples are drawn from the gas stream before hydrogen is added to it.

Organic Sulfur Other Than Carbon Disulfide

The concentration of the total organic sulfur shows a consistent excess of sulfur contained in these products over that contained in the carbon disulfide. This excess amounted to 2.8 grains of sulfur per 100 cubic feet of gas in Table II and to 8.5 grains in Table III. Furthermore, this excess is shown consistently in all experiments in which organic sulfur is formed and shows that sulfur compounds other than carbon disulfide are formed by the decomposition of the carbon-sulfur complex.

The exact nature of the organic sulfur compounds, other than carbon disulfide, formed by this decomposition of the complex was not determined. It is probable, however, that in these experiments the compounds were carbon monosulfide and carbon subsulfide, C_3S_2. The formation of carbon monosulfide has been studied by Dewar and Jones (50, 51),* whose experiments show that the compound exists as a gas. This gas could not be collected as such because at this concentration the compound rapidly polymerized into a solid product. The presence of an inert gas retarde this polymerization. In such concentrations as are encountered in these experiments the carbon monosulfide should, there-

fore, exist as a gas. Since the pure compound cannot be isolated as a gas, no specific test for it has been developed.

*See page 13.

The existence and composition of the carbon subsulfide has been verified (54).** It can be prepared by decomposing carbon disulfide in a quartz tube at a high temperature and is collected as a red liquid at ordinary temperatures. This compound also exhibits a tendency to polymerize slowly into a solid product, but its physical properties as a liquid, including vapor pressure, are reported. Its vapor pressure is only 1 mm. at 20° C. and 2 mm. at 30° C. These considerations indicate that carbon subsulfide may be present under the experimental conditions used in the study reported herein, but its presence could not be proved, as no specific test for it has been reported.

**See page 14.

Sulfur Content of Charcoal Residue

The difference in the concentration of sulfur in the charcoal residues of the two experiments is not of significance. Sulfur containing residues of carbon cannot be prepared experimentally with identical concentrations of sulfur (26).* This sulfur of the residue is retained as a carbon-sulfur complex and the experimental evidence shows that the formation of the complex is a surface reaction.** Therefore, any change in conditions which causes a change in the surface of the charcoal (per unit weight of the charcoal) presented to the action of sulfur containing gases will cause a change in the percentage of sulfur retained by the charcoal.

*Wibaut and La Bastide, see page 8.
**See qualitative experiments, pp. 31-2.

The quantities of charcoal selected for the two experiments were different in order that the total surface of the charcoal should be different. The fact that the concentration of carbon disulfide in the gas was the same for these changed conditions supports the hypothesis of the formation of an intermediate product, the carbon-sulfur complex. That is, the formation of carbon disulfide takes place according to the reaction:

$$C+S_2=C_xS_y=CS_2.$$

Since the complex, C_xS_y, is a solid product, the vapor pressure of the carbon disulfide given off by it is independent of its concentration, and therefore independent of the concentration of sulfur in the charcoal residue from the experiments.

CHAPTER VIII

THE CHANGE IN THE CONCENTRATION OF ORGANIC SULFUR WITH CHANGES IN THE CONDITIONS OF ITS FORMATION

During the manufacture of gas it is often necessary to change the conditions of manufacture to provide for even operation of the plant, to meet peak load requirements or to take care of variations in the quality of the raw materials used. As a result of such changes in operation, the amount and quality of the gas often varies. That such changes affect the concentration of organic sulfur in raw works gas has been observed by Craven and Dunkley (7),* who have reported that the organic sulfur content of the gas bears no definite relation to the sulfur content of the raw materials used. There is included in this dissertation, therefore, an examination of the effect of varying conditions upon the formation of organic sulfur.

*See page 3.

The factors relating to the formation of organic sulfur that are reported herein are the effect of changes in temperature, concentration of hydrogen and hydrogen sulfide, and the effect of the presence of carbon monoxide, oxygen and water vapor. In order to discuss the effect of these factors, the experiments at 1500° F. reported in Chapter VII have been used as a basis for comparison.

Effect of Temperature

Several experiments were made using different temperatures but retaining for the reacting gas nitrogen mixed with a small volume of hydrogen sulfide. The gas stream was dried with phosphorous pentoxide before it was passed over the charcoal. The conditions were maintained as nearly as possible the same as those used at 1500° F. except for the temperature of the charcoal. The results at 1600° F. are given in Table IV and those at 1700° F. in Table V.

The increase in the concentration of carbon disulfide with an increase in temperature is very definite. The excess of sulfur in the total organic sulfur over that in the carbon disulfide is shown in the experiment at 1700° F. The carbon disulfide in the experiments at 1500 and 1700° F. constitutes from 70 to 90 per cent of the total organic sulfur when based on the sulfur content of these substances.

The percentage of sulfur contained in the charcoal residue showed no significant variation with the change in temperature. The reasons for this have been explained.*

*See page 40.

TABLE IV

DATA OF EXPERIMENT 10 [a]

Time	H_2S entering the reaction tube—grains per 100 cu. ft. of gas	H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	CS_2 in gas leaving the reaction tube—grains CS_2 per 100 cu. ft. of gas
11.15 A. M.	445	69	....
12.15 P. M.	455	227	....
1.15	445	247	....
1.30	*	*	....
2.15	445	257	....
3.15	435	247	....
4.15	435	247	....
5.05	...	...	79.0
5.15	435	257	....
6.15	435	257	....
8.00	435	257	....
8.20	...	...	84.9
9.00	445	247	....
10.00	445	257	....
10.20	...	...	80.3
11.00	445	257	....
Average	443	...	81.4

REMARKS: Reacting gas: Nitrogen containing hydrogen sulfide, dried with phosphorous pentoxide.

Temperature of charcoal: 1600° F.

Rate of gas flow at charcoal: 0.59 cu. ft. per hour.

Sulfur in charcoal residue: 3.87% (by weight).

a No values of total organic sulfur were recorded because the supply of available hydrogen was completely exhausted, due to a leaky valve on the storage cylinder. This fact was not discovered until the experiment had been started.

* Gas sample drawn at this time examined for oxygenated products, particularly CO. These were not detected.

TABLE V

DATA OF EXPERIMENT 9

Time	H_2S entering the reaction tube—grains per 100 cu. ft. of gas	H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	Total organic sulfur in gas at the spiral —grains H_2S per 100 cu. ft. of gas	Total organic sulfur in gas leaving the reaction tube —grains H_2S per 100 cu. ft. of gas	CS_2 in gas leaving the reaction tube —grains CS_2 per 100 cu. ft. of gas
11.00 A. M.	483	178	19.7	37.2	....
12.00 Noon	483	256	45.4	85.9	....
1.00 P. M.	483	266	53.3	100.9	....
2.00	473	266	55.2	104.2	....
3.00	473	276	....	.....	....
4.00	473	256	63.2	119.7	....
5.00	473	266	59.2	112.0	....
5.05	...	...	....	.....	98.6
6.00	473	256	61.2	115.7	....
8.00	...	256	....	.....	....
8.25	...	...	....	.....	100.6
9.00	473	256	61.2	115.7	.....
10.00	...	256	59.2	112.0	.....
10.15	...	...	....	.....	109.8
11.00	463	256	55.2	104.2	.....
Average	473	...	....	111.9*	103.0

REMARKS: Reacting gas: Nitrogen containing hydrogen sulfide, dried with phosphorous pentoxide.
Temperature of charcoal: 1700° F.
Rate of gas flow at charcoal: 0.58 cu. ft. per hour.
Analysis of gas leaving spiral: 47.1% H_2, 52.9% N_2 (by volume).
Sulfur in charcoal residue: 3.03% (by weight).
* Average includes values from 2.00 P. M. only.

From the results of these experiments it is concluded that under conditions of gas manufacture where the carbon-sulfur complex is active in the formation of organic sulfur products an increase in the concentration of carbon disulfide and other organic sulfur compounds may be expected.

Effect of Increased Concentration of Hydrogen Sulfide

An experiment was made in which the concentration of the hydrogen sulfide in the reacting gas was increased. The results are given in Table VI.

During this experiment some trouble was experienced in maintaining the gas flow at a constant rate due to the increased tendency to deposit free sulfur caused by the increase in concentration of hydrogen sulfide. The results indicate, however, that there has resulted an increase in concentration of carbon disulfide and of sulfur compounds other than carbon disulfide. The percentage of carbon disulfide in the total organic sulfur decreased to about 67.5.

It is concluded from this experiment that an increase in the concentration of hydrogen sulfide present, when the carbon-sulfur complex is active in the formation of organic sulfur, causes an increase in the concentration of organic sulfur in the gas.

Effect of Water Vapor

The experiment at 1500° F. was repeated with the phosphorous pentoxide tower replaced by a two-inch water seal. The contact of the gas with this water seal saturated it with water vapor at 31° C. Water vapor reacts with charcoal at this temperature according to the water gas reactions and thus may be expected to alter the conditions of formation of the complex. The results of the experiment are given in Table VII.

The total organic sulfur formed at this temperature did not change. The concentration of carbon disulfide decreased, indicating that an increased concentration of other organic sulfur compounds is present. A portion of this increase in organic sulfur compounds other than carbon disulfide is probably due to the formation of carbon oxysulfide. Carbon monoxide and dioxide are formed by the reaction of water vapor and charcoal at this temperature. Both of these substances react with sulfur to form carbon oxysulfide at this temperature.*

*See page 13.

The percentage of sulfur contained in the charcoal residue is greater than that found in any other experiment. The reaction of the water vapor with the charcoal results in a decrease in the particle size of the charcoal, thus increasing the area of surface per unit weight of charcoal exposed to the action of the gas. Since the formation of the car-

TABLE VI

DATA OF EXPERIMENT 12

Time	H_2S entering the reaction tube—grains per 100 cu. ft. of gas	H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	Total organic sulfur in gas at the spiral—grains H_2S per 100 cu. ft. of gas	Total organic sulfur in gas leaving the reaction tube—grains H_2S per 100 cu. ft. of gas	CS_2 in gas leaving the reaction tube—grains CS_2 per 100 cu. ft. of gas
10.30 A. M.	782	317	13.9	26.0	....
11.30	773	555	15.8	29.5	....
12.30 P. M.	763	555	25.8	48.2	....
1.30	753	535	23.8	44.5	....
2.30	743	535	27.8	52.0	....
3.30	733	525	29.7	55.5	....
4.30	714	525	24.8	46.4	....
5.30	714	515	27.8	52.0	....
7.15	704	535	17.8	*a*	....
8.15	704	525	23.8	44.5	....
8.25	...	...	....	....	37.7
9.45	684	505	29.7	55.5	....
10.45	684	...	26.8	50.1	....
11.10	...	...	....	....	39.1
12.00	674	...	25.8	48.2	....
Average*	690	...	....	49.6	38.4

REMARKS: Reacting gas: Nitrogen containing hydrogen sulfide dried with phosphorous pentoxide.
Temperature of charcoal: 1500° F.
Rate of gas flow at charcoal: 0.52 cu. ft. per hour.
Analysis of gas leaving spiral: 46.5% H_2, 53.5% N_2 (by volume).
Sulfur in charcoal residue: 3.62% (by weight).
* All averages taken from 7.15 P. M. only.
a This value discarded as being incorrect.

TABLE VII

DATA OF EXPERIMENT 8

Time	H_2S entering the reaction tube—grains per 100 cu. ft. of gas	H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	Total organic sulfur in gas at the spiral —grains H_2S per 100 cu. ft. of gas	Total organic sulfur in gas leaving the reaction tube —grains H_2S per 100 cu. ft. of gas	CS_2 in gas leaving the reaction tube —grains CS_2 per 100 cu. ft. of gas
11.20 A. M.	523	217	7.9	14.6	....
12.20 P. M.	533	375	11.8	21.8	....
1.20	533	405	11.8	21.8	....
2.20	543	424	13.8	25.5	....
3.20	543	444	13.8	25.5	....
4.20	543	464	17.8	32.9	....
5.20	543	454	17.8	32.9	....
6.50	543	464	17.8	32.9	....
7.05	...	...	....	....	23.6
7.50	533	464	17.8	32.9	....
8.50	533	454	17.8	32.9	....
9.00	...	...	....	....	24.6
9.50	533	454	15.8	29.2	....
10.50	...	454	17.8	32.9	....
11.00	...	...	....	....	24.0
11.50	533	454	17.8	32.9	....
Average	538	...	....	32.9	24.1

REMARKS: Reacting gas: Nitrogen containing hydrogen sulfide, saturated with water vapor at 31° C.
Temperature of charcoal: 1500° F.
Rate of gas flow at charcoal: 0.57 cu. ft. per hour.
Analysis of gas leaving spiral: 45.8% H_2, 54.2% N_2 (by volume).
Sulfur in charcoal residue: 6.09% (by weight).

bon-sulfur complex is a surface phenomenon, this increase in the percentage of sulfur is to be expected in the experiment.

In the manufacture of gas the presence of water vapor in contact with the carbon-sulfur complex may be expected to cause an increase in the concentration of the organic sulfur compounds other than carbon disulfide.

Effect of Carbon Monoxide

The gas used in this experiment was obtained from a blast gas collected during the blasting period of a water gas machine. This gas was first passed through the copper gauze, then scrubbed with a strong solution of caustic potash to remove the carbon dioxide before the hydrogen sulfide was added. The gas was then dried with phosphorous pentoxide.

From the analysis of the original gas it was calculated that the residual gas, after removing the carbon dioxide, contained 16.5 per cent carbon monoxide, the remainder of the gas being nitrogen. In order to check the accuracy of the analysis, the composition of this residual gas was also determined from the analyses made on the gas collected at the outlet of the platinum spiral. These showed 16.4 and 16.0 per cent carbon monoxide.

The original gas was examined for organic sulfur compounds, but no trace could be detected.

The experimental results are presented in Table VIII.

During this experiment there was a gradual increase in the concentration of the hydrogen sulfide in the reacting gas going to the charcoal. This increase is probably due to the fact that the last traces of the carbon dioxide contained in the blast gas were removed in the sodium hydrosulfide solution used for the generation of hydrogen sulfide. This causes an increase in the hydrogen ion concentration of the solution with a resulting increase in the concentration of hydrogen sulfide which appears in the gas. Because of this condition an equilibrium was not reached during this experiment.

Although an equilibrium was not reached, the increase in the concentration of organic sulfur compounds other than carbon disulfide is so great that this cannot be ascribed to any experimental condition other than the presence of the carbon monoxide in the reacting gas. Carbon monoxide is known to react readily with sulfur vapor at this temperature to form carbon oxysulfide,* and it is probable that the increase in organic sulfur concentration is due to the formation of this compound.

*See page 13.

The sulfur content of the residue from this experiment decreased considerably. Due to the formation of carbon oxysulfide it is probable that the partial pressure of sulfur vapor in the gas mixture is decreased over that in other experiments. It has already been pointed out that the sulfur content of these residues is to a certain extent dependent upon

TABLE VIII

DATA OF EXPERIMENT 5

Time	P. M. 1.30	2.15	2.45	3.15	3.45	4.00	5.15	7.15	7.50	8.30	Average
H_2S entering the reaction tube—grains per 100 cu. ft. of gas	417	446	456	466	485	....	515	563	....	592	*
H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	194	291	320	340	350	....	388	427	....	446	*
Total organic sulfur in gas at the spiral—grains H_2S per 100 cu. ft. of gas	31.1	54.5	56.4	56.4	56.4	....	62.2	68.0	....	72.0	*
Total organic sulfur in gas leaving the reaction tube grains H_2S per 100 cu. ft. of gas	54.1	94.8	98.1	98.1	98.1	....	108.1	118.3	....	125.2	*
CS_2 in gas leaving the reaction tube—grains CS_2 per 100 cu. ft. of gas	....	....	....	....	....	19.1	....	....	36.2	....	*

REMARKS: Reacting gas: 10.2% CO_2, 14.8% CO, 0.0% O_2, 75.0% N_2 (by volume). The CO_2 was scrubbed from the gas before contact with the charcoal and the residue dried with phosphorous pentoxide. Theoretical analysis of gas over charcoal: 16.5% CO, 83.5% N_2 (by volume).

Temperature of charcoal: 1500° F.

Rate of gas flow at charcoal: 0.56 cu. ft. per hour.

Analysis of gas leaving the spiral: 42.5% H_2, 9.3% CO, 48.2% N_2 (by volume). Calculated analysis of residual gas: 16.2% CO, 83.8% N_2 (by volume).

Sulfur in charcoal residue: 1.46% (by weight).

Note: The reacting gas was examined for organic sulfur, but no trace was detected.

* No average values calculated because of variations in conditions of experimentation.

the concentration of sulfur compounds in the gas.** These sulfur compounds dissociate at high temperatures to yield a partial pressure of sulfur vapor which is probably the active factor in the formation of such sulfur containing residues.

**See page 9.

The results of this experiment indicate that the presence of carbon monoxide and sulfur compounds during the manufacture of gas results in the formation of an increased concentration of organic sulfur compounds. It should be remembered that this experiment was carried out on a gas which had been dried over phosphorous pentoxide, and that in commercial practice the gas in reaction would contain some steam. The presence of steam might alter the formation of the organic sulfur compounds, particularly if these consist largely of carbon oxysulfide, which interacts with steam (129).

Effect of Oxygen

One of the samples of nitrogen supplied for use in this work was found to contain about 3.6 per cent oxygen, the remainder being nitrogen. This percentage was too great for the copper gauze to remove completely throughout the duration of the experiment. This condition caused a slowly increasing percentage of oxygen in the gas reacting with the charcoal. Before the experiment was completed the concentration of the oxygen in the gas after the copper gauze had attained 3.6 per cent. The results of the experiment are reported in Table IX.

The oxygen favored the formation of organic sulfur compounds other than carbon disulfide. The oxygen reacted with the charcoal, which reaction yields both carbon dioxide and monoxide. It has already been explained that these substances may react with sulfur vapor to give carbon oxysulfide.*

*See page 53.

The hydrogen sulfide in the gas was burned to sulfur dioxide. Before the experiment was completed a test of the outlet gas with a lead acetate stain paper did not show any hydrogen sulfide.

There was an insufficient amount of charcoal left at the end of the experiment to allow a determination of the concentration of sulfur. There was a small quantity of ash remaining in the reaction tube.

In the manufacture of gas it is probable that the presence of oxygen leads to the formation of carbon monoxide and dioxide, which in turn react with the sulfur present to favor the formation of organic sulfur compounds such as carbon oxysulfide rather than carbon disulfide.

Effect of Hydrogen

Several experiments were made using hydrogen mixed with a small volume of hydrogen sulfide. The gas was used dry and saturated with

TABLE IX

DATA OF EXPERIMENT 4

Time	Noon 12.00	P. M. 12.30	1.00	1.30	2.00	2.30	3.00	4.00	5.00	5.30	8.30	Average.
H_2S entering the reaction tube—grains per 100 cu. ft. of gas	349	359	....	378	378	....	388	388	....	....	408	*
H_2S leaving the reaction tube—grains per 100 cu. ft. of gas	145†	145	165	204	252	....	291	349	378	....	398	....
Total organic sulfur in gas at the spiral—grains H_2S per 100 cu. ft. of gas	....	13.3	21.6	29.1	31.1	....	27.2	23.3	27.2	....	....	....
Total organic sulfur in gas leaving the reaction tube—grains H_2S per 100 cu. ft. of gas	....	23.2	37.8	50.9	54.4	....	47.5	40.8	47.5	....	....	*
CS_2 in gas leaving the reaction tube—grains CS_2 per 100 cu. ft. of gas	....	....	....	....	....	8.7	....	....	....	**	....	*

REMARKS: Reacting gas: 3.6% O_2, 96.4% N_2 (by volume), dried with phosphorous pentoxide. At the end of the experiment a gas sample drawn after the reaction tube showed this same percentage, O_2.

Temperature of charcoal: 1500° F.

Rate of gas flow at charcoal: 0.68 cu. ft. per hour.

Analysis of gas leaving the spiral: Contained, 42.8% H_2 (by volume).

Sulfur in charcoal residue: The charcoal was completely burned leaving a small amount of ash.

* No average values calculated because of variation in the conditions of experimentation.

** CS_2 sample lost before analysis was completed. Portion of sample showed the presence of CS_2.

† These readings are partly SO_2. At 3.30 P. M. no trace of H_2S could be detected in the outlet gas, using a lead acetate paper.

water vapor at temperatures from 1500 to 1900° F., but in no case was the presence of carbon disulfide or any other organic sulfur compound detected in the gas. The concentration of hydrogen sulfide at the outlet of the reaction tube was the same as that at the inlet. The charcoal residue contained only 0.46 per cent of sulfur, so that no appreciable amount of sulfur remained unaccounted for.

It is probable that the formation of carbon disulfide follows the reaction of free sulfur vapor and carbon. Under the conditions of experimentation the partial pressure of free sulfur vapor was very low because of the retardation of the dissociation of hydrogen sulfide by the high partial pressure of hydrogen. The reverse process, where the carbon-sulfur complex already formed is destroyed by the action of hydrogen, has been reported by Powell (29, 30).* The sulfur of the complex is removed quantitatively as hydrogen sulfide by the action of pure hydrogen at high temperatures. When gases are used which are not pure hydrogen, the complete removal of sulfur is not effected.

*See page 9.

The experiments involving hydrogen were continued, using for the gas stream a mixture containing 24.5 per cent hydrogen, the remainder being nitrogen with a small volume of hydrogen sulfide. The experimentally determined concentrations of hydrogen sulfide at the inlet and outlet of the reaction tube accounted for all the sulfur contained in the gas. The tests for organic sulfur at the spiral were negative. When the gas was tested for carbon disulfide, using Huff's method (118), a very slight trace of cupric xanthate could be collected on a filter paper after allowing the solution to stand overnight.

The charcoal residue from this experiment was found to contain 0.76 per cent sulfur, indicating that the decreased concentration of hydrogen in the reacting gas allowed the formation of the complex to begin.

The action of hydrogen during the manufacture of gas is then to retard the formation of organic sulfur from the carbon-sulfur complex. In applying the foregoing observations to commercial gas making operations, it must be remembered that the time of contact in the ordinary equipment is extremely short and the conditions are heterogeneous. Such conditions mean that the complex present may decompose in a region where there is a temporary excess of sulfur yielding organic sulfur which is not subsequently decomposed because of the short time of contact or because of the possibility that the gases may be stratified in the machine and thus the organic sulfur may not come into contact with the hydrogen necessary to transform it into hydrogen sulfide. This has already been discussed by Huff (15),* who showed that the rapid heating of coal, with the consequent short time of contact, gave carbon disulfide, even though the gases contained a high percentage of hydrogen. When the heating was slow, with longer time of contact, this carbon disulfide did not appear.

*See page 5.

While true equilibria are thus not often reached in commercial practice, data on the equilibria values under various conditions such as temperature and concentration are very useful because such values indicate trends which permit some prediction of changes which may accompany changes in temperature or other conditions.

CHAPTER IX

THERMODYNAMICS OF THE FORMATION OF CARBON DISULFIDE

The thermodynamical data available on the formation of carbon disulfide is rather limited, and some of it has been criticized as being incorrect. This limitation has led Lewis and Randall (43) to state: "It seems inadvisable, until new equilibrium data or new calorimetric data have been obtained, to attempt to set up a general equation for the free energy of formation of carbon disulfide." The data presented in this dissertation support some of the criticisms that have been made of previous work, so it seemed advisable to examine the data more completely from a thermodynamical standpoint, and particularly so since the data on the formation of carbon disulfide are so limited.

The formation of carbon disulfide from sulfur vapor and graphite at high temperatures has been studied by Koref (42). The reaction was considered to be $C+S_2=CS_2$, the equilibrium constant, K, was expressed as the ratio $(S_2)/(CS_2)$. The following values of the equilibrium constant were given by him:

Temperature °C.	100 K.
906	11.5±0.23
1009	17.9±0.12
1110	25.8±0.19

These values were used by Koref in an integrated form of Nernst's reaction isochore,

$$Q=\frac{4.571\cdot T_1\cdot T_2\ (\log K_2-\log K_1)}{T_2-T_1},*$$

to calculate the heat of reaction Q. The value obtained was +12,500 calories, indicating that the reaction is exothermic.

*In this equation T represents absolute temperatures Centigrade. The factor 4.571 is the product of the gas constant, R, in small calories, times 2.3026 to convert from natural logarithms to logarithms with 10 as the base, thus giving Q in small calories. The reaction isochore and its integrated form are given in Nernst, "Theoretical Chemistry, 1916, pp 688-9 (Translated by Tizard and revised in accordance with the seventh German edition).

During an investigation of the equilibrium between carbon oxysulfide, carbon monoxide and sulfur vapor, Lewis and Lacey (43) found among the products of the reaction carbon disulfide and another sulfur

compound which they believed to be carbon monosulfide. As a result of this they pointed out that Koref's work, while thermodynamically consistent *inter se*, is inconsistent with other thermodynamical data on the reaction. They have also contended that: " . . . the heat of reaction obtained by Koref is erroneous not only in magnitude but probably also in sign." ** They suggest that an error is introduced by neglecting the formation of compounds of carbon and sulfur other than carbon disulfide, which appear at the temperatures which Koref used. The experimental data presented on preceding pages prove the presence of a sulfur compound or compounds other than carbon disulfide under conditions very similar to those used by Koref. In view of this fact, and because of the existing controversy, it seemed desirable to attempt a calculation of the equilibrium constant of the reaction from the experimental data developed in this dissertation.

**See Lewis and Randall (43).

Preliminary considerations showed that it would be difficult to calculate data from experiments in which oxygenated compounds were present. The reactions involved are necessarily complex, and it becomes difficult to predict completely the changes taking place. Moreover, the low partial pressures of the constituents involved make it difficult to introduce approximations without danger of causing large errors in the final results.

In the experiments which involved only hydrogen sulfide and carbon in the presence of nitrogen the possible reactions are somewhat limited. The only disturbing factor of note in these experiments appeared to be a slight partial pressure of hydrogen resulting from the decomposition of hydrogen sulfide. Furthermore, the amount of sulfur contained in the reaction products other than carbon disulfide is known, and in view of this it was felt that the partial pressure of sulfur vapor could be calculated from these data with a fair degree of accuracy.

The application of any calculations presented in this chapter is, of course, limited by the accuracy used in securing the data involved. It should be remembered that the data were secured primarily to indicate the course of some of the reactions of importance in the formation of organic sulfur compounds under gas making conditions. Under these conditions a true equilibrium is probably not reached. The experimental apparatus was designed to give equilibria by the flow method, and many tests indicated that equilibria were reached, but experiments leading to the establishment of static equilibria were not conducted. Free sulfur was deposited in the outlet capillary, which at times caused some difficulty in maintaining a constant rate of gas flow.

The approximate equilibrium constants for the reaction $C+S_2=CS_2$ have been calculated from the results presented in Tables II, III, IV, V and VI. The results are given in Table X.

TABLE X *

EQUILIBRIUM CONSTANTS FOR THE REACTION $C+S_2=CS_2$

Data of Table	Temperature °F.	°T.	1/T.	$K=(CS_2)/(S_2)$
II	1500	1089	0.0009182	0.177
III	1500	1089	0.0009182	0.183
VI	1500	1089	0.0009182	0.199
IV	1600	1144	0.0008741	0.598**
V	1700	1200	0.0008333	0.634

* The calculations of these values are illustrated in the Appendix.
** See following paragraphs.

These constants have been calculated on the assumption that the gases followed the perfect gas laws and therefore the partial pressures of the gases are directly proportional to their concentrations. The partial pressure of sulfur vapor was calculated from the concentration of hydrogen sulfide in the gas, using the dissociation constants determined by Preuner and Schupp, and also by Randall and Bichowsky (130). The dissociation calculations were corrected for the sulfur used up in the formation of organic sulfur compounds other than carbon disulfide.

A word of explanation should be given regarding the calculation of the constants at 1600 and 1700° F. The data for the experiment at 1600° F. was incomplete, as no values of the total organic sulfur concentration were obtained.* This value was estimated from the remaining experiments upon the assumption that the carbon disulfide contains an average of about 80 per cent of the sulfur found in the total organic sulfur.

*See Table IV.

At the end of the experiment of 1700° F. the concentration of carbon disulfide was still increasing,** and it was quite apparent that none but the last value obtained should be used in the calculation of the constant, so this was taken.

**See Table V.

Considering the limitations under which the study was made, the agreement for the values of the equilibrium constant at 1500° F. is good. The conditions used for the three experiments at this temperature were all quite different.

It is believed that these measurements permit a safe prediction of the sign of the heat of the reaction at these temperatures. The data presented indicate that the reaction is endothermic, that is, it absorbs heat from the surroundings, which is contrary to the finding of Koref. This supports the contention of Lewis and Lacey.***

***See pages 58-9.

Since there also exists the question regarding the magnitude of the heat of reaction, this was calculated from the equilibrium constants. In order to make these calculations, it was assumed that the molar specific heat at constant pressure of carbon disulfide could be represented by that for carbon dioxide, sulfur vapor by that for oxygen,* and charcoal by that of graphite.** There exists some question of the reproducibility of the properties of the amorphous forms of carbon, since they usually contain small percentages of hydrogen. Debrunner (131) reports that the specific heats of the amorphous forms of carbon are indistinguishable and that the specific heat of purified wood charcoal agrees quite closely with that of graphite even below 600° C.

*For these values see Lewis and Randall, "Thermodynamics," 1923, 1st ed., p. 80.
**Same reference, p. 569.

The calculation of the heat of reaction from the equilibrium constants at 1500 and 1600° F. was not used because of the doubt concerning the concentration of the total organic sulfur. However, this data is sufficiently accurate to predict that the heat of reaction is endothermic.

Using the constants at 1500 and 1700° F. the heat of reaction is $\triangle H_{298} = +26{,}117$ calories.***

This value of +26,117 calories agrees quite closely with that obtained from calorimetric determinations, but this may be a coincidence without significance.

***These calculations are illustrated in the Appendix. The heat of reaction is expressed using the system of Lewis and Randall (see "Thermodynamics," 1923, 1st ed., p. 98). A positive value for $\triangle H$ thus shows the reaction to be endothermic.

CHAPTER X

THE DISTRIBUTION OF SULFUR DURING THE CRACKING OF OIL AND THE EFFECT OF METALS ON THIS DISTRIBUTION

In some gas making processes oil is used as a raw material. As it usually contains some sulfur, a portion of this element appears in the gaseous products. It is desirable to know how much may be expected in the gaseous products and how it is distributed between the inorganic and organic sulfur forms. From the data developed in Chapter VI, that in the organic form is believed to originate, in part, at least, from the decomposition of the carbon-sulfur complex. The complex normally decomposes to give up sulfur in an organic form, but in the presence of a gas containing a high percentage of hydrogen it may decompose to give hydrogen sulfide, particularly when this gas contains no sulfur originally. Under gas making conditions both forms of sulfur appear. Since a rather high concentration of hydrogen is present during the cracking of oil at the temperatures used in gas making, it may be possible to speed up the decomposition of the complex with the formation of hydrogen sulfide by catalysis without speeding up the formation of organic sulfur. This was attempted by introducing a metal at the point of decomposition of the complex.

Apparatus

The apparatus used for this study was essentially the same as that in Figure 1, with the gasometer replaced by the apparatus necessary to use the platinum spiral, as illustrated in Figure 2. A sampling tee, R, of Figure 2, was used after the tar filter for withdrawing samples for the determination of the hydrogen sulfide content of the oil gas. In the spiral train the gas was conducted directly from the washing bottle, T, to the spiral, U, and this was followed by the sampling tee, washing bottle and meter, as shown in Figure 2.

During the course of the experiments it was found advantageous to use in an approximately vertical rather than a horizontal position the vitreosil tube in which the cracking takes place. If the tube was placed in a completely vertical position the oil dropped through without vaporizing appreciably. For this reason the tube was inclined from the vertical plane just enough to allow the oil to impinge on the side of the tube in the heated zone. The vitreosil tube was 36 inches long and ⅞-inch inside diameter. This tube was heated by two electric furnaces, each having an effective heating length of one foot.

Procedure

The experiments described in this chapter were carried out at a cracking rate of 1 cc. of oil every five minutes. The heating current was turned on and the furnaces brought up to the desired temperature before beginning to crack the oil. The temperature was measured by base metal thermocouples placed between the cracking tube and the furnace wall. The hydrogen sulfide formed during the cracking was removed from the gas before it reached the platinum spiral by passing the gas through two seals of saturated cadmium chloride solution in series.

During the experiments, the gas generated was tested for the concentration of hydrogen sulfide and total organic sulfur. The hydrogen sulfide was determined in a 100 cc. Tutwiler burette by titration with an iodine solution, 1 cc. of which represented 100 grains of hydrogen sulfide per 100 cubic feet of gas.

For the determination of the hydrogen sulfide formed from the decomposition of the organic sulfur by the spiral, this iodine solution was diluted to one-tenth the strength given above. Each cc. of this diluted solution represented 10 grains of hydrogen sulfide per 100 cubic feet of gas when used in a 100 cc. Tutwiler burette, and 1 cc. of this same diluted solution represented 2 grains of hydrogen sulfide per 100 cubic feet of gas when used in a 500 cc. Tutwiler burette. In most of the experiments, the organic sulfur content of the gas was sufficiently high to permit the use of a 100 cc. Tutwiler burette for the determination.

Decomposition on the Platinum Spiral

The high temperature required on the platinum spiral to insure complete decomposition of the organic sulfur also caused some decomposition of the rich gas formed by cracking the oil. This fact was shown by the deposition of tar in the pyrex tube containing the spiral. It is probable that a slight error is introduced in the determination of the concentration of organic sulfur by this decomposition, which probably causes a slight increase in the gas volume. The tar deposited in the tube containing the spiral was examined for sulfur, which it might contain as a result of the decomposition of the gas, but no trace was detected.

In calculating the sulfur distribution, the increased gas volume produced by the decomposition at the spiral introduces a slight error in the sulfur estimated as hydrogen sulfide. This error does not appear in the result obtained for the sulfur existing as organic sulfur because the volume of gas is measured after the spiral.

Sulfur Distribution During the Cracking of Oil

In the first experiments the gas oil described in Table I was cracked at different temperatures and the distribution of sulfur in the products of reaction was noted. The results of these experiments are given in

TABLE XI

EFFECT OF TEMPERATURE ON THE DISTRIBUTION OF SULFUR DURING CRACKING OF OIL

Temperature °F.	Position of cracking tube	Gas yield cu. ft. per c.c. of oil	H_2S content of gas—grains per 100 cu. ft.	Organic sulfur—grains H_2S per 100 cu. ft.
1350	Horizontal	0.0123	1170	6.8
1600	Horizontal	0.0212	870	70.7
1600	Vertical	0.0233	994	61.7

	Per Cent of Total Sulfur in Oil as		
H_2S	Organic sulfur	Tar	Coke
26.9	0.14	49.7	4.8
33.9	2.77	....	6.1
42.8	2.66	....	...

REMARKS: None of the experiments were continued for longer than three hours. The individual data from which this table was made showed that equilibrium conditions had not been reached. The results are, however, considered indicative since equilibrium conditions are not reached in the usual commercial units.

Table XI. The distribution of the sulfur in each of the major products of the reaction will be discussed individually.

Hydrogen Sulfide

The concentration of hydrogen sulfide in the gas decreased as the temperature of the cracking increased. This may be accounted for, in part, at least, by the increase in volume of gas when the temperature is increased. Although the concentration of the hydrogen sulfide decreased the percentage by weight of the sulfur as hydrogen sulfide increased with the temperature.

Organic Sulfur

The concentration and the percentage by weight of the sulfur appearing as organic sulfur both increased with the temperature. The weight increase in this case was relatively much greater than that of hydrogen sulfide.

Tar

A part of the tar formed at 1350° F. could be collected as a liquid and it is the sulfur contained in this portion that is reported. Some of the tar was, of course, taken up by the cotton used as a tar filter. At 1600° F. all of the tar was retained by the filter which was not extracted to recover the tar. This consequently explains a rather large part of the unaccounted-for sulfur.

Coke

The percentage of sulfur contained in the coke collected in the cracking tube was lower at the increased temperature. The increased quantity of coke recovered at the higher temperature accounts for the increase in the total amount of sulfur which it contains. The coke could not be recovered completely, and this accounts for some of the missing sulfur. It should be noted that these limitations on the recovery of sulfur are not imposed upon the sulfur contained in the gas.

That the coke deposited during the cracking of oil contains sulfur touches upon an interesting point brought up by Klein (16) in his discussion of a water gas machine modified to use a high-coke, high-sulfur oil for carburetting the gas.* He reported that a large proportion of the sulfur in the oil did not appear in the gas when the temperature of the checker brick in the machine was properly regulated. From his description of the operation of the machine this sulfur must be retained by the carbon deposited on the checker brick during the run and subsequently disappears during the following blow when this carbon is destroyed by combustion.

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*See page 7.

The Solution of Metallic Compounds in the Oil

As explained in the introduction to this chapter, the experiments were continued with oil containing a metal. In order to deposit this metal at the complex, it was incorporated into the oil in a form which would break down at the temperature of cracking and free the metal through the reducing action of the gases present. The metals were incorporated in the oil as the oleates.

These were prepared by allowing the precipitated oxides of the desired metals to react with slightly more than the required stoichiometric amount of free oleic acid. It was necessary to heat the acid and to add the oxide to the heated acid gradually in order to allow the water formed by the reaction to escape without loss of the products. When the reaction was complete, the products were cooled to a temperature just sufficient to maintain them liquid and the desired quantity of gas oil was added. The resulting mixture was placed in a water bath at 90° C. and allowed to remain, with frequent agitation, for at least one hour. The mixture was then allowed to cool to room temperature. When prepared in this way, the product was entirely uniform and free-flowing, and exhibited no tendency to deposit the added oleate even after standing for several months.

Mixtures were prepared containing 150 cc. of oil and sufficient oleate to give one gram of iron, zinc or copper. A fourth solution was prepared in which oleate containing 2 grams of copper was added to 150 cc. of oil.

Results of Cracking Oil Containing Metals

The mixtures described above were cracked at 1600° F., and the gas formed was examined for hydrogen sulfide and organic sulfur. The experiments with the oil containing copper are indicative of the general results, and are given in Table XII.

The effect of the copper was not only to decrease the concentration of the sulfur products in the gas, but also to decrease the total amount of sulfur contained in these products. The reduction with iron and with zinc was not so great, and for a lack of space these results are therefore not presented here.

The method of calculating the percentages of the sulfur in the products requires some explanation. The addition of the oleate to the oil causes a slight reduction in the percentage of sulfur in the mixture when referred to the percentage in the original oil. This may have some effect on the concentration of the sulfur in the gas formed, but a corrected sulfur content of the oil-oleate mixture was used in the calculation of the percentage of sulfur appearing in the gas. The correction was calculated from the weight of oleate added to the oil and the weight of oil. The weight of oil was calculated from its volume and specific gravity. For the final calculations it was assumed that the specific gravity of the oil containing the oleate was the same as that of the original oil. The calculated specific gravity of the oil-oleate mix-

TABLE XII

EFFECT OF COPPER ON THE DISTRIBUTION OF GASEOUS SULFUR AT 1600° F.

Oil used contains per 150 c.c.	Position of cracking tube	Gas yield cu. ft. per c.c. of oil	H_2S content of gas—grains per 100 cu. ft.
No metal	Vertical	0.0233	994
1 gram Cu.	Vertical	0.0232	777
2 grams Cu.	Vertical	0.0231	644

Organic sulfur grains H_2S per 100 cu. ft.	Per Cent of Total Sulfur in Oil as H_2S	organic sulfur
61.7	42.8	2.66
40.9	35.7	1.88
33.1	31.6	1.62

REMARKS: None of these experiments were continued longer than three hours.

ture was so little different from that of the original oil that any error introduced from this assumption is negligible.

Variations in the Concentrations of Sulfur Products in Gas

The variations in the concentrations of the sulfur forms during an experiment are quite interesting. Curves illustrating these variations are shown in Figure 3 and represent the experiments given in Table XII.

The variations in the concentration of hydrogen sulfide and of organic sulfur during the cracking of oil containing no metal are very marked. It is believed that, since the cracking tube was free from carbon at the beginning of the experiment, the decrease in the concentration of hydrogen sulfide is due to the adsorption of sulfur by the carbon deposited during the cracking. This adsorbed sulfur ultimately forms the carbon-sulfur complex. This view is supported by the increasing concentration of organic sulfur. As the formation of the complex proceeds, this concentration should increase and finally reach a uniform value. It is possible that all of the organic sulfur may not be attributed to this source, since the concentration of this at the beginning of the experiment did not indicate that it had zero concentration when no complex was present. However, it may be possible to deposit the complex directly as a product of the cracking, but this could not be proved. These observations were verified by other experiments, the results of which it was not deemed necessary to report.

These curves show very clearly the effect of the copper in reducing the concentrations of hydrogen sulfide and of organic sulfur. Furthermore, the concentrations have assumed a nearly constant value. The trend of the hydrogen sulfide concentration is slightly increasing, while that of the organic sulfur is slightly decreasing. This may indicate that the metal was having some effect in catalyzing the decomposition of the complex to give hydrogen sulfide rather than organic sulfur products.

It is also possible that the presence of the metal during the cracking caused the deposition of an increased quantity of carbon. This carbon would adsorb sulfur and may account for the reduction in the concentration of sulfur appearing as gaseous products. The data of these experiments do not furnish sufficient evidence to verify this explanation.

These general results were also observed when zinc was used instead of copper. When iron was used it was observed that the concentrations of the sulfur products in the final gas were quite low. The cause for this was found in the increased volume of gas formed during this experiment, the increase amounting to 13 per cent. The total sulfur contained in the gas was greater than that contained in gas formed from oil having the same weight of copper and cracked at the same temperature.

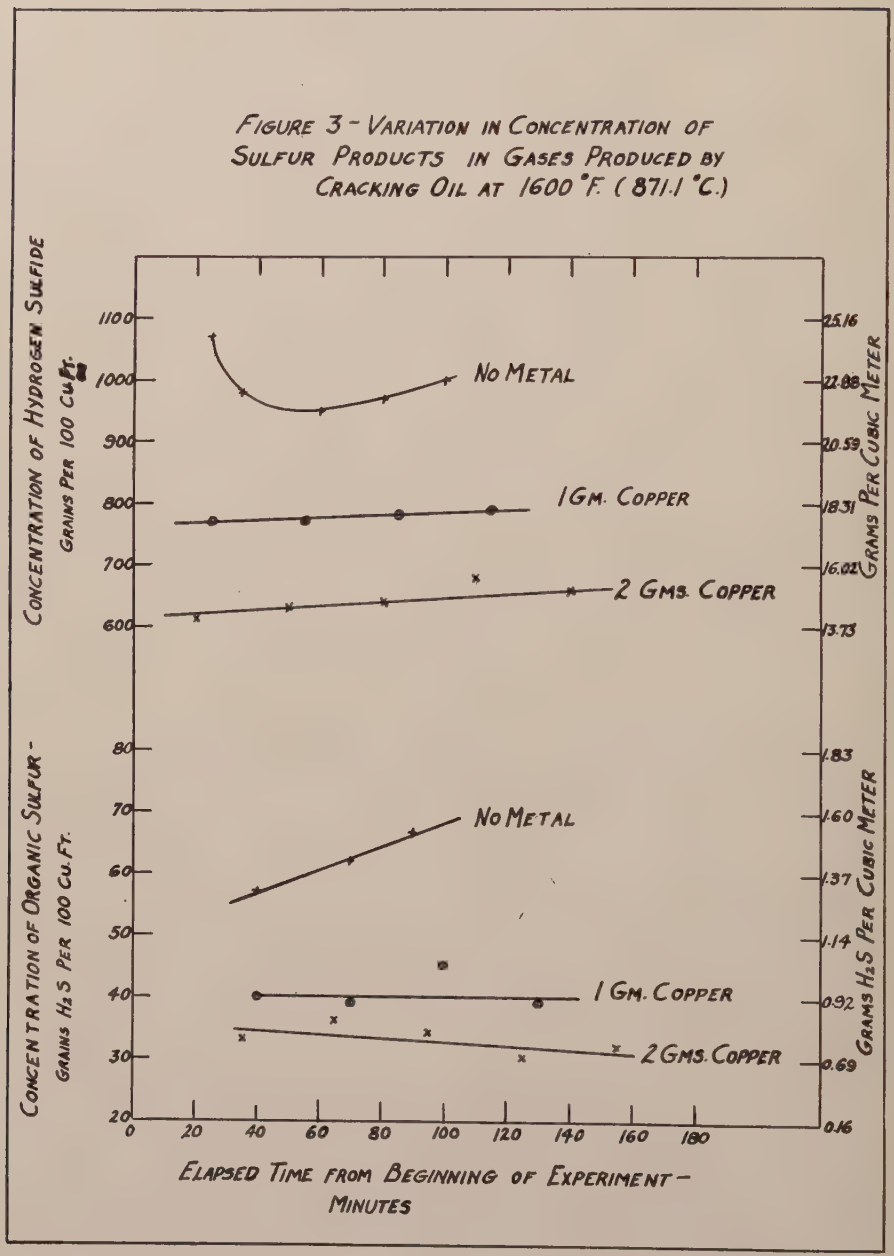
FIGURE 3 - VARIATION IN CONCENTRATION OF SULFUR PRODUCTS IN GASES PRODUCED BY CRACKING OIL AT 1600 °F. (871.1 °C.)
CONCENTRATION OF HYDROGEN SULFIDE GRAINS PER 100 CU. FT.
CONCENTRATION OF ORGANIC SULFUR - GRAINS H2S PER 100 CU. FT.
GRAMS PER CUBIC METER
GRAMS H2S PER CUBIC METER
NO METAL
1 GM. COPPER
2 GMS. COPPER
NO METAL
1 GM. COPPER
2 GMS. COPPER
1100
1000
900
800
700
600
80
70
60
50
40
30
20
25.16
22.88
20.59
18.31
16.02
13.73
1.83
1.60
1.37
1.14
0.92
0.69
0.16
0
20
40
60
80
100
120
140
160
180
ELAPSED TIME FROM BEGINNING OF EXPERIMENT - MINUTES

SUMMARY

The literature relating to (1) the occurrence of organic sulfur in gas and studies of its control, (2) the association of carbon and sulfur in a solid product, (3) compounds of carbon and sulfur which may be expected in gas, (4) the removal of organic sulfur from gas, and (5) methods of determining the concentration of carbon disulfide and total organic sulfur in gas has been reviewed.

Experimental work on the cracking of a gas oil containing 3.61 per cent sulfur showed that carbon disulfide may be expected in the gaseous products if a temperature of 1200° F. is exceeded. Carbon disulfide was also formed during the cracking of a sulfur free oil in the presence of a gas from this same oil to which hydrogen sulfide was added. An important loss of sulfur to products other than carbon disulfide was noted.

Nitrogen containing a small volume of hydrogen sulfide was passed over sugar charcoal, free from sulfur, and heated to incandescence. For a short time no hydrogen sulfide could be detected in the gas after contact with the charcoal, but this sulfide did subsequently appear and its concentration slowly increased. After more gas had passed, carbon disulfide appeared as a product of the reaction. The charcoal residue was found to contain sulfur, and the concentration of this was greater in the case where the surface per unit weight of charcoal exposed to the action of the gas was greater.

The effect of heated terminal surfaces of pumice or charcoal free from sulfur in removing organic sulfur was examined. When the deposition of carbon and sulfur on these surfaces was allowed to increase these ultimately became ineffective for the removal.

These results led to the conclusion that the organic sulfur results from a complex formed by the action of sulfur on carbon. This complex has been called the carbon-sulfur complex.

This theory of the formation of organic sulfur by the decomposition of the carbon-sulfur complex was examined under equilibrium conditions by passing nitrogen containing hydrogen sulfide over heated sugar charcoal in an apparatus designed to cool the reaction products without much reversion. The complex gave off carbon disulfide and other organic sulfur compounds. These other compounds were not identified, but the concentration of sulfur which they contained was determined.

These experiments were continued in order to examine the effect of different factors on this formation of gaseous organic sulfur from the complex. The factors examined were temperature, concentration of hydrogen sulfide, saturation of the reacting gas with water vapor at room temperature, and the presence of carbon monoxide, oxygen or hydro-

gen. An increase in temperature or concentration of hydrogen sulfide caused an increase in the concentration of total organic sulfur formed as well as that of carbon disulfide. The presence of carbon monoxide or oxygen caused an increase in the concentration of organic sulfur, the increase taking place principally in compounds other than carbon disulfide. Hydrogen caused a decrease in the concentration of organic sulfur. Water vapor did not affect the concentration of the total organic sulfur appreciably, but reduced that of carbon disulfide.

The equilibrium constant for the formation of carbon disulfide from carbon and sulfur vapor was calculated from the experimental results. This data verified the fact that the reaction absorbs heat, that is, it is endothermic. The heat of reaction was calculated, and this agreed with previous data which has been secured from calorimetric measurements.

The formation of organic sulfur compounds during the cracking of oil was examined further and the distribution of sulfur in the products of the cracking reported. The effect of metals incorporated in the oil as oleates on this distribution was also reported. The metals caused a reduction in the percentage by weight of sulfur which appears in the gas.

The variation of the concentration of hydrogen sulfide and organic sulfur during the cracking of oil which contained no metal supported the theory of the role of the carbon-sulfur complex in the formation of organic sulfur. The organic sulfur concentration increased steadily during the experiment, while that of hydrogen sulfide decreased rapidly at first, and then increased slowly. The presence of a metal caused these concentrations to maintain a very nearly constant value throughout the experiment, there being no large variations from the initial concentrations.

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APPENDIX

THERMODYNAMICAL CALCULATIONS USED IN OBTAINING THE DATA PRESENTED IN CHAPTER IX*

The calculation of the equilibrium constant, K, for the reaction $C+S_2=CS_2$, was made from the partial pressures of the reacting gases. These partial pressures were calculated using the assumption that the reacting gases obey the perfect gas laws and therefore the partial pressures are proportional to the concentrations of the gases. This is, of course, at least approximately true.

The concentrations of the pure gases are:

$$H_2S=\frac{100\times28.317\times15.43\times34.08}{22.4}=66{,}470 \text{ grains/100 cu. ft.}$$

$$S_2=\frac{100\times28.317\times15.43\times64.128}{22.4}=125{,}090 \text{ grains/100 cu. ft.}$$

$$CS_2=\frac{100\times28.317\times15.43\times76.128}{22.4}=148{,}490 \text{ grains/100 cu. ft.}$$

K From Table II

$$\text{Partial pressure of } H_2S=\frac{517}{66{,}470}=0.007777 \text{ atmosphere.}$$

$$\text{Partial pressure of } S_2 \text{ vapor used in formation of organic sulfur}=\frac{32.064\times 29.1}{34.080\times125{,}090}=0.0002189 \text{ atm.}$$

$$\text{Partial pressure of } CS_2=\frac{29.2}{148{,}490}=0.0001966 \text{ atm.}$$

The dissociation of H_2S may be represented by the reaction:

$$H_2+\tfrac{1}{2}S_2=H_2S.$$

The equilibrium constant, K^1, for this reaction has been determined as

$$\frac{(H_2S)}{(H_2)\ (S_2)^{\frac{1}{2}}}$$

using the partial pressures of the reacting gases. The values of K^1 at

*It is recognized that any calculations involving the heat of reaction of carbon disulfide are limited in validity because of the lack of fundamental specific heat data. Furthermore, as demonstrated, other compounds of carbon and sulfur are formed at the time of reaction. Although these limitations were recognized, it seemed desirable to present these as preliminary data for the benefit of those who may be interested ir further inquiry.

different temperatures are given in Lewis and Randall "Thermodynamics," 1923, 1st ed., p. 299. At 1500° F.

$$K^1 = 57.75.$$

In calculating the partial pressure of sulfur vapor let X = the partial pressure of H_2S lost by dissociation, then X = the partial pressure of H_2 formed by dissociation, and ½X = the partial pressure of S_2 formed by dissociation. Substituting these values in the expression

$$K^1 = \frac{(H_2S)}{(H_2)\ (S_2)^{1/2}} \qquad (1)$$

$$57.75 = \frac{0.007777 - X}{X(\frac{1}{2}X - 0.0002189)^{1/2}}$$

solving, X = 0.0026593 atm.

Then the effective partial pressure of S_2 at equilibrium:

$$\frac{0.0026593 - 0.0002189 = 0.001111 \text{ atm.}}{2}$$

$$K_{1500} = \frac{(CS_2)}{(S_2)} = \frac{0.0001966}{0.001111} = 0.177 \qquad (2)$$

K From Table III

$$\text{Partial pressure } H_2S = \frac{527}{66{,}470} = 0.007928 \text{ atm.}$$

$$\text{Partial pressure of } S_2 \text{ vapor used in formation of organic sulfur} = \frac{32.064 \times 35.7}{34.080 \times 125{,}090} = 0.0002670 \text{ atm.}$$

$$\text{Partial pressure } CS_2 = \frac{29.8}{148{,}300} = 0.0002007 \text{ atm.}$$

Substituting in equation (1),

$$57.75 = \frac{0.007928 - X}{X(\frac{1}{2}X - 0.000267)^{1/2}}$$

solving, X = 0.002727 atm.

Effective partial pressure of S_2 at equilibrium:

$$\frac{0.002727 - 0.000267 = 0.001097 \text{ atm.}}{2}$$

$$K_{1500} = \frac{(CS_2)}{(S_2)} = \frac{0.0002007}{0.001097} = 0.183 \qquad (3)$$

K From Table VI

$$\text{Partial pressure } H_2S = \frac{690}{66{,}470} = 0.01029 \text{ atm.}$$

Partial pressure of S_2 vapor used in formation of organic sulfur=

$$\frac{32.064 \times 49.6}{34.080 \times 125{,}090} = 0.0003738 \text{ atm.}$$

Partial pressure $CS_2 = \frac{38.4}{148{,}300} = 0.0002586$ atm.

Substituting in equation (1),

$$57.75 = \frac{0.01029 - X}{X(\frac{1}{2}X - 0.0003738)^{\frac{1}{2}}}$$

solving, X = 0.003345 atm.

Effective partial pressure of S at equilibrium:

$$\frac{0.003345 - 0.0003738}{2} = 0.001299 \text{ atm.}$$

$$K_{1500} = \frac{(CS_2)}{(S_2)} = \frac{0.0002586}{0.001299} = 0.199 \qquad (4)$$

K From Table IV

Partial pressure $H_2S = \frac{443}{66{,}470} = 0.006694$ atm.

Since no values for the concentration of total organic sulfur were recorded in this experiment, it is assumed that the carbon disulfide contains 80 per cent by weight of the sulfur in the total organic sulfur.

Partial pressure of S_2 vapor used in formation of organic sulfur=

$$\frac{64.128 \times 81.4}{76.128 \times 0.8 \times 125{,}090} = 0.0006852 \text{ atm.}$$

Partial pressure $CS_2 = \frac{81.4}{148{,}490} = 0.0005482$ atm.

$$K'_{1600} = 35.97$$

Substituting in equation (1),

$$35.97 = \frac{0.006694 - X}{X(\frac{1}{2}X - 0.0006852)^{\frac{1}{2}}}$$

solving, X = 0.0032042 atm.

Effective partial pressure of S_2 at equilibrium:

$$\frac{0.0032042 - 0.0006852}{2} = 0.0009169 \text{ atm.}$$

$$K_{1600} = \frac{(CS_2)}{(S_2)} = \frac{0.0005482}{0.0009169} = 0.598$$

K From Table V

Partial pressure $H_2S = \frac{473}{66{,}470} = 0.0071305$ atm.

Partial pressure of S_2 vapor used in formation of organic sulfur=

$$\frac{32.064 \times 111.9}{34.080 \times 125{,}090} = 0.0008417 \text{ atm.}$$

Partial pressure $CS_2 = \frac{109.8}{148{,}300} = 0.0007394$ atm.

$$K^1_{1700} = 23.08$$

Substituting in equation (1),

$$23.08 = \frac{0.0071305 - X}{X(\frac{1}{2}X - 0.0008417)^{\frac{1}{2}}}$$

solving, $X = 0.0040154$ atm.

Effective partial pressure of S_2 at equilibrium:

$$\frac{0.0040154 - 0.0008417}{2} = 0.001166 \text{ atm.}$$

$$K_{1700} = \frac{(CS_2)}{(S_2)} = \frac{0.0007394}{0.001166} = 0.634 \qquad (5)$$

CALCULATION OF THE HEAT OF REACTION

The variation of the equilibrium constant, K, with a change in absolute temperature, T, is given by the equation:

$$\frac{4.5787 \text{ d log } K}{\text{d } (1/T)} = -\triangle H \text{ *} \qquad (6)$$

The symbol $\triangle H$ represents the heat of reaction at the temperature, T.

The variation of the heat of reaction, $\triangle H$, with absolute temperature, T, is expressed by the equation:

$$\triangle H = \triangle H_0 + \triangle \lceil_0 T + \tfrac{1}{2} \triangle \lceil_1 T^2 + \tfrac{1}{3} \triangle \lceil_2 T^3 \text{ **} \qquad (7)$$

In this equation $\triangle H_0$ is a constant of integration, and would be the heat of reaction at absolute zero, if the equation were valid to this temperature, which is seldom, if ever, the case. The values of $\triangle \lceil_0$, $\lceil \triangle_1$, etc., are determined from the sum of the specific heat formulas of the products minus the sum of the specific heat formulas for the reactants.

Substituting equation (7) in (6) and integrating we get:

$$-4.5787 \log K = \frac{\triangle H_0 - \triangle \lceil_0 (2.3026) \log T - \tfrac{1}{2} \triangle \lceil_1 T - \tfrac{1}{6} \triangle \lceil_2 T^2 + I}{T} \qquad (8)$$

The value of $\triangle \lceil_0$, etc., is calculated in the following manner:

The reaction is assumed to be:

$$C + S_2 = CS_2$$

$$C_p \ CS_2 \text{ (use } CO_2) = 7.0 + 0.00710 \ T - 0.00000186 \ T^2$$

$$C_p \ C \text{ (use graphite)} = 1.1 + 0.00048 \ T - 0.00000120 \ T^2$$

$$C_p \ S_2 \text{ (use } 0_2) = 6.5 + 0.00100 \ T$$

*See Lewis and Randall, "Thermodynamics," 1923, 1st ed., p. 298.

**See Lewis and Randall, "Thermodynamics," 1923, 1st ed., p. 103.

Adding equations (10) and (11) and subtracting from (9)

$$\Delta C_p = -0.6 + 0.00562\ T - 0.00000066\ T^2$$

From this value of ΔC_p we take the following values:

$$\Delta \lceil_0 = -0.6$$
$$\Delta \lceil_1 = +0.00562$$
$$\Delta \lceil_2 = -0.00000066$$

Substituting these values in equation (8),

$$-4.5787 \log K = \frac{\Delta H_0}{T} + 1.38156 \log T - 0.00281\ T + 0.00000011\ T^2 + I \qquad (12)$$

Substituting in equation (12), an average value of K from (2), (3), and (4) at 1500° F. (1089° T.) we get

$$-4.5787 \log 0.186 = \frac{\Delta H_0}{1089} + 1.38156 \log 1089 - 0.00281 \times 1089 + 0.00000011 \times 1089^2 + I$$

Solving,

$$\frac{\Delta H_0}{1089} = +2.07862 - I \qquad (13)$$

Substituting in equation (12), the value of K from (5) at 1700° F. (1200° T.) and solving, we get

$$\frac{\Delta H_0}{1200} = -0.13425 - I \qquad (14)$$

Eliminating I between equations (13) and (14),

$$\Delta H_0 = +26{,}052 \text{ calories.}$$

Substituting the values of ΔH_0 and $\Delta \lceil_0$, $\Delta \lceil_1$ and $\Delta \lceil_2$ in equation (7)

$$\Delta H = +26{,}052 - 0.6\ T + 0.00281\ T^2 - 0.00000022\ T^3$$

Solving this equation at 25° C. (298° T.),

$$\Delta H_{298} = +26{,}117 \text{ calories.}$$

The reaction at room temperature is therefore endothermic, that is, it absorbs heat from its surroundings.

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BIOGRAPHICAL NOTE

John Cromwell Holtz, son of John and Nannie Cromwell (Hodgkin) Holtz, was born in Baltimore, Maryland, on October 31, 1904. He attended the grade schools of Baltimore and was graduated from the Baltimore Polytechnic Institute in June, 1922. He entered the Johns Hopkins University in September, 1923, and received the degree of Bachelor of Science in Chemistry in June, 1926. His work for an advanced degree was begun in the Department of Gas Engineering at the Johns Hopkins University in September, 1926.

Before entering upon his university studies, he was employed as a laboratory assistant with the Baltimore Tube Company from September, 1922, to May, 1923, after which he served in the same capacity in the laboratories of the United States Asphalt Refining Company until September, 1923. During the summers, he was employed by the United States Asphalt Refining Company in 1924 and by the Consolidated Gas Electric Light and Power Company of Baltimore in 1925, 1926, 1927 and 1928.

While engaged in his regular work as a graduate student in the Department of Gas Engineering, he has also served as Student Assistant during the academic years 1926-27 and 1927-28. During 1928-29 he served as a Junior Instructor in his Department, and is serving in the same capacity during 1929-30.

He is a member of the American Chemical Society, Sigma Xi, and Tau Beta Pi.